

## DECLARATION

I, Kyoko Fujimoto of c/o SHIGA INTERNATIONAL PATENT OFFICE, Gran Tokyo South Tower 1-9-2 Marunouchi, Chiyoda-ku, Tokyo 100-6620 JAPAN, understand both English and Japanese, am the translator of the English document attached, and do hereby declare and state that the attached English document contains an accurate translation of the official certified copy of Japanese Patent Application No(s).2004-134585 and that all statements made herein are true to the best of my knowledge.

Declared in Tokyo, Japan

*This 17<sup>th</sup> day of September, 2008*

*Kyoko Fujimoto*

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Kyoko Fujimoto

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Applicant(s) : Tokyo Ohka Kogyo Co., Ltd.

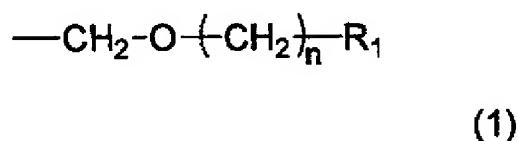
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(Inventor)	
(Address)	c/o TOKYO OHKA KOGYO CO., LTD., 150, Nakamaruko, Nakahara-ku, Kawasaki-shi, Kanagawa-ken, Japan;
(Name)	Toshiyuki OGATA
(Inventor)	
(Address)	c/o TOKYO OHKA KOGYO CO., LTD., 150, Nakamaruko, Nakahara-ku, Kawasaki-shi, Kanagawa-ken, Japan;
(Name)	Syogo MATSUMARU
(Inventor)	
(Address)	c/o TOKYO OHKA KOGYO CO., LTD., 150, Nakamaruko, Nakahara-ku, Kawasaki-shi, Kanagawa-ken, Japan;
(Name)	Hideo HADA
(Inventor)	
(Address)	c/o TOKYO OHKA KOGYO CO., LTD., 150, Nakamaruko, Nakahara-ku, Kawasaki-shi, Kanagawa-ken, Japan;
(Name)	Hiroaki SHIMIZU
(Inventor)	
(Address)	c/o TOKYO OHKA KOGYO CO., LTD., 150, Nakamaruko, Nakahara-ku, Kawasaki-shi, Kanagawa-ken, Japan;
(Name)	Naotaka KUBOTA
(Applicant for Patent)	
(Identification Number)	000220239
(Name)	TOKYO OHKA KOGYO CO., LTD.
(Agent)	
(Identification Number)	100106909
(Patent Attorney)	
(Name)	Sumio TANAI
(Agent)	
(Identification Number)	100064908
(Patent Attorney)	
(Name)	Masatake SHIGA
(Elected Agent)	
(Identification Number)	100101465
(Patent Attorney)	
(Name)	Masakazu AOYAMA
(Elected Agent)	
(Identification Number)	100094400
(Patent Attorney)	
(Name)	Mitsuyoshi SUZUKI
(Elected Agent)	
(Identification Number)	100106057
(Patent Attorney)	
(Name)	Noriko YANAI
(Official Fee)	
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[Document Type] Claims

[Claim 1]

- A polymer compound comprising:  
 an alkali soluble group (i), wherein  
 5 at least one hydrogen atom of the alkali soluble group (i) is substituted by an acid  
 dissociable, dissolution inhibiting group (ii) represented by a general formula (1):



- (wherein R<sub>1</sub> represents a cycloaliphatic group which contains no more than 20 carbon  
 atoms, and n represents 0 or an integer of 1 to 5.), and  
 10 the polymer compound exhibits changed alkali solubility under the action of an acid.

[Claim 2]

A polymer compound according to claim 1, wherein the alkali soluble group (i)  
 is at least one selected from an alcoholic hydroxyl group, a phenolic hydroxyl group, or a  
 carboxyl group.

15 [Claim 3]

A polymer compound according to claim 2, wherein a carbon atom adjacent to  
 the carbon atom bonded to the alcoholic hydroxyl group is bonded to at least one fluorine  
 atom.

[Claim 4]

- 20 A polymer compound according to any one of claims 1 to 3, wherein the  
 cycloaliphatic group contains an adamantane backbone.

[Claim 5]

A polymer compound according to any one of claims 1 to 4, wherein R<sub>1</sub>  
 represents the cycloaliphatic group containing at least one hydrophilic group.

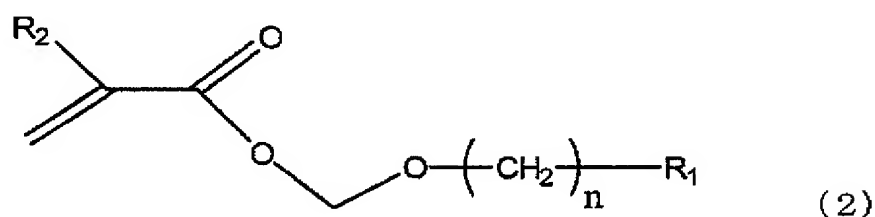
25 [Claim 6]

A polymer compound according to claim 5, wherein the hydrophilic group is at

least one selected from the group consisting of a carbonyl group, an ester group, an alcoholic hydroxyl group, ether, an imino group, and an amino group.

[Claim 7]

A compound represented by a general formula (2):



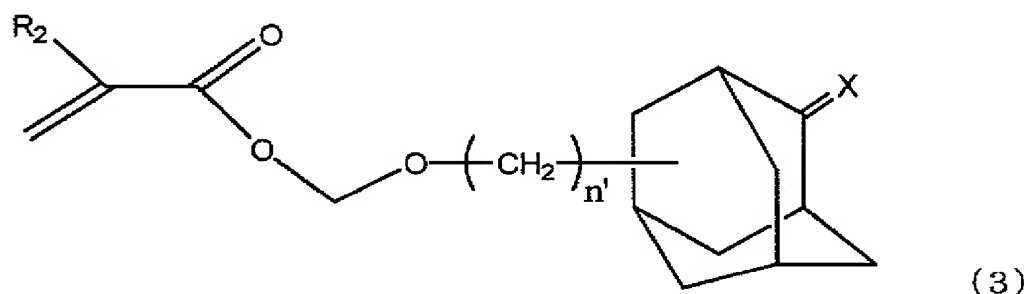
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(wherein  $\text{R}_1$  and  $n$  represents the same as the aforementioned; and  $\text{R}_2$  represents a hydrogen atom, a fluorine atom, a lower alkyl group containing more than 20 carbon atoms, or a fluorinated lower alkyl group containing more than 20 carbon atoms.).

[Claim 8]

10

A compound according to claim 7, represented by a general formula (3):



(wherein  $\text{R}_2$  represents the same as the aforementioned,  $\text{X}$  represents two hydrogen atoms or an oxygen atom, and  $n'$  represents 0 or 1.).

[Claim 9]

15

A polymer compound according to any one of claims 1 to 6, comprising a structural unit (a1) derived from the compound according to claim 7 or 8.

[Claim 10]

A polymer compound according to claim 9, further comprising a structural unit (a3) derived from (meth)acrylate containing a lactone-containing monocyclic or

polycyclic group.

[Claim 11]

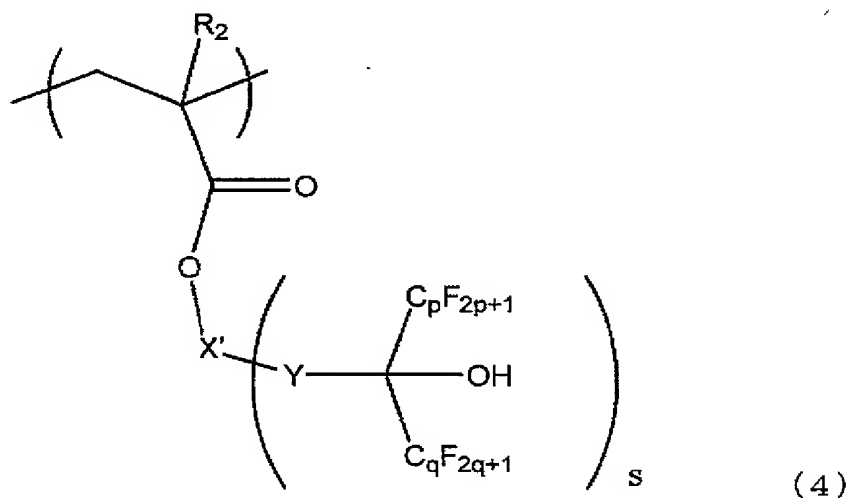
A polymer compound according to claim 10, wherein the structural unit (a3) comprises at least two mutually different structural units derived from (meth)acrylate containing a lactone-containing monocyclic or polycyclic group.

[Claim 12]

A polymer compound according to claim 10 or 11, further comprising a structural unit (a4) derived from (meth)acrylate containing a polar group-containing polycyclic group.

10 [Claim 13]

A polymer compound according to claim 9, further comprising a structural unit (a6) represented by a general formula (4):



15 (wherein  $\text{R}_2$  represents the same as the aforementioned,  $\text{X}'$  represents a divalent or trivalent cyclic group,  $\text{Y}$  represents an alkylene or alkyloxy group containing 1 to 6 carbon atoms which is divalent,  $p$  and  $q$  independently represent an integer of 1 to 5, and  $s$  represents an integer of 1 or 2.).

[Claim 14]

20 A photoresist composition comprising:  
a base material resin component (A) which exhibits changed alkali solubility

under the action of an acid; and

an acid generator component (B) which generates the acid on exposure to radiation, wherein

the base material resin component (A) is the polymer compound according to  
5 any one of claims 1 to 6, or 9 to 13.

[Claim 15]

A photoresist composition according to claim 14, further comprising a nitrogen-containing organic compound (D).

[Claim 16]

10 A resist pattern formation method comprising:  
forming a photoresist film on a substrate using the photoresist composition according to claim 14 or 15;

exposing the photoresist film; and

developing the photoresist film to form a resist pattern.



[Document Type] Specification

[Title of the Invention] POLYMER COMPOUND, PHOTORESIST COMPOSITION INCLUDING THE POLYMER COMPOUND, AND RESIST PATTERN FORMATION METHOD

5

[Field of the Invention]

[0001]

The present invention relates to a polymer compound; a low molecular weight compound which is preferable for preparing the polymer compound; a photoresist  
10 composition including the polymer compound; and a resist pattern formation method.

[Background Art]

[0002]

It is no exaggeration that miniaturization of a semiconductor integrated circuit  
15 pattern has been accomplished due to the progress of photolithography and peripheral techniques thereof. This photolithography includes two generally known main techniques. One is a technique on an exposure wavelength or a numerical aperture of a reduction projection exposure apparatus known as a stepper or a scanner. The other is a technique on resist characteristics such as printing resolution of a photoresist composition  
20 in which a mask pattern is printed by the aforementioned reduction projection exposure apparatus. These have improved processing accuracy of a semiconductor integrated circuit pattern by means of photolithography.

[0003]

The wavelength of light sources used in the reduction projection exposure  
25 apparatus has been increasingly shortened in response to a demand for high resolution circuit patterns. In general, the g-line (436 nm) or i-line (365 nm) of a mercury lamp is used in the case of a resist resolution of about 0.5 $\mu$ m or 0.30 to about 0.5  $\mu$ m, respectively. The main spectra of the g-line and i-line are 436 nm and 365 nm, respectively. Also, a KrF excimer laser (248 nm) and an ArF excimer laser (193 nm) are used in the case of a

resist resolution of 0.15 to about 0.30  $\mu\text{m}$ , or about 0.15  $\mu\text{m}$  or less, respectively. Furthermore, use of an  $\text{F}_2$  excimer laser (157 nm), an  $\text{Ar}_2$  excimer laser (126 nm), and EUV (extreme ultraviolet light, wavelength: 13 nm) is being investigated in order to further miniaturize a semiconductor integrated circuit pattern.

5 [0004]

As far as a photoresist composition is concerned, the life of a photoresist for KrF in lithography using a KrF excimer laser is currently prolonged by combining this photoresist with an organic or inorganic anti-reflective film or by devising an exposure system, and the photoresist composition with an eye to about 110 nm, which is below  $\lambda/2$ ,  
10 is being developed. Also, provision of a photoresist composition for ArF has been desired, which is preferable for the mass production of a prospective fine pattern with a node of about 90 nm or less in lithography using an ArF excimer laser. Furthermore, lithography using the aforementioned  $\text{F}_2$  excimer laser has drawn attention as a technique for processing a prospective fine pattern with a node of 65 nm or less, and a photoresist  
15 composition is being developed which is applicable to fine processing by lithography using an  $\text{F}_2$  excimer laser.

[0005]

Since it is difficult for a conventional positive photoresist including an alkali soluble novolak resin and a quinone diazide group-containing compound as main  
20 components to achieve such a fine pattern, a resist applicable to a far-UV ray with a further shortened wavelength (200 to 300 nm); an excimer laser such as KrF, ArF, or  $\text{F}_2$ ; an electron beam; and X ray has been desired to be developed. As such a resist, a chemically amplified resist has drawn attention and is being actively developed, in which a catalytic reaction and a chain reaction due to an acid generated on exposure to radiation  
25 can be realized, the quantum yield is 1 or higher, and high resolution and sensitivity can be achieved.

[0006]

A resin containing an acid dissociable, dissolution inhibiting group is mainly used in a positive chemically amplified resist.

Examples of an acid dissociable, dissolution inhibiting group used in the chemically amplified resist include an acetal group, a tertiary alkyl group such as a tert-butyl group, tert-butoxycarbonyl group, and tert-butoxycarbonylmethyl group as an acid dissociable, dissolution inhibiting group for a fluorinated alcohol as disclosed in the following non-patent references 1 to 3.

[0007]

Also, as described in the following patent reference 1, a structural unit derived from a tertiary ester compound of (meth)acrylic acid, for example 2-alkyl-2-adamantyl (meth)acrylate, is generally used as a structural unit containing an acid dissociable, dissolution inhibiting group in a resin component of a conventional ArF resist composition.

[Non-patent reference 1]

T. Hagiwara, S. Irie, T. Itani, Y. Kawaguchi, O. Yokokoji, S. Kodama, J. Photopolym. Sci. Technol. Vol. 16, Page 557, 2003

[Non-patent reference 2]

F. Houlihan, A. Romano, D. Rentkiewicz, R. Sakamuri, R. R. Dammel, W. Conley, G. Rich, D. Miller, L. Rhodes, J. McDaniels, C. Chang, J. Photopolym. Sci. Technol. Vol. 16, Page 581, 2003

[Non-patent reference 3]

Y. Kawaguchi, J. Irie, S. Kodama, S. Okada, Y. Takebe, I. Kaneko, O. Yokokoji, S. Ishikawa, S. Irie, T. Hagiwara, T. Itani, Proc. SPIE, Vol. 5039, Page 43, 2003

[Patent reference 1]

Japanese Unexamined Patent Application, First Publication No. Hei8-320105

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

[0008]

However, an acid dissociable, dissolution inhibiting group used in these chemically amplified resists disclosed in non-patent references 1 to 3 has a problem in

terms of the improvement of resolution and the formation of a fine pattern with a good rectangularity because an alkali dissolution inhibiting effect in a unexposed part is insufficient (thickness loss occurs in a resist pattern.). Provided that an introduction rate of an acid dissociable, dissolution inhibiting group is increased to improve an alkali  
5 dissolution inhibiting effect in a unexposed part, there is another problem in that the risk of defect is increased.

[0009]

Also, as described in the patent reference 1, a compound forming a cyclic or linear tertiary alkyl ester with a carboxyl group of (meth)acrylic acid is well-known as a  
10 compound forming an acid dissociable, dissolution inhibiting group. However, there is a limitation to the number of types of an available acid generator. In other words, there is a problem of not working as a chemically amplified positive resist because an acid dissociable, dissolution inhibiting group is not dissociated unless an acid generator is used, in which acid strength of a generated acid is strong, for example an onium salt containing  
15 a fluorinated alkylsulfonic acid ion at an anion part. Also, there is another problem in that sensitivity is not sufficient when an acid generator is used, in which acid strength of a generated acid is weak. The improvement of these problems has highly been desired.

[0010]

The present invention has been accomplished in consideration of the  
20 aforementioned problems, and an object of the present invention is to provide a polymer compound which can constitute a photoresist composition capable of having an excellent resolution, forming a fine pattern with a favorable rectangularity, obtaining favorable resist characteristics even when acid strength of an acid generated from an acid generator is weak, and having favorable sensitivity. Also, other objects of the present invention  
25 are to provide a compound preferable for preparing the polymer compound, a photoresist composition including the polymer compound, and a resist pattern formation method using the photoresist composition.

[Means for Solving the Problem]

[0011]

To achieve the aforementioned objects, the present inventors have conducted intensive research in which various acid dissociable, dissolution inhibiting groups were introduced into an alkali soluble group of a polymer compound for a photoresist composition as a protecting group, and the resist characteristics of these polymer compounds were investigated. Then, for the first time, it was found in the case of using an acid dissociable, dissolution inhibiting group containing a specific cycloaliphatic group that a fine pattern with a favorable resist pattern shape and improved resolution can be formed. The present invention has been completed on the basis of the above knowledge.

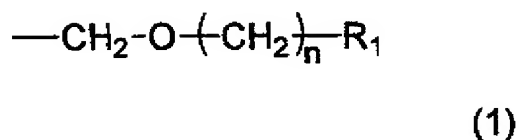
In addition, it was also found in the case of using an acid dissociable, dissolution inhibiting group containing a specific cycloaliphatic group that more choices of an acid generator and a highly sensitive resist composition can be obtained in comparison with the case of forming an acid dissociable, dissolution inhibiting group by using a conventional compound which forms a cyclic or linear tertiary alkylester with a carboxyl group of (meth)acrylic acid.

[0012]

A polymer compound of present invention includes an alkali soluble group (i), wherein at least one hydrogen atom of the alkali soluble group (i) is substituted by an acid dissociable, dissolution inhibiting group (ii) represented by a general formula (1):

[0013]

[Chem 1]



[0014]

(wherein R<sub>1</sub> represents a cycloaliphatic group which contains no more than 20 carbon atoms, and n represents 0 or an integer of 1 to 5.), and the polymer compound exhibits changed alkali solubility under the action of an acid.

It is preferable that the alkali soluble group (i) be at least one selected from an alcoholic hydroxyl group, a phenolic hydroxyl group, or a carboxyl group. When the alkali soluble group (i) is an alcoholic hydroxyl group, it is more preferable that a carbon atom adjacent to the carbon atom bonded to the alcoholic hydroxyl group be bonded to at least one fluorine atom.

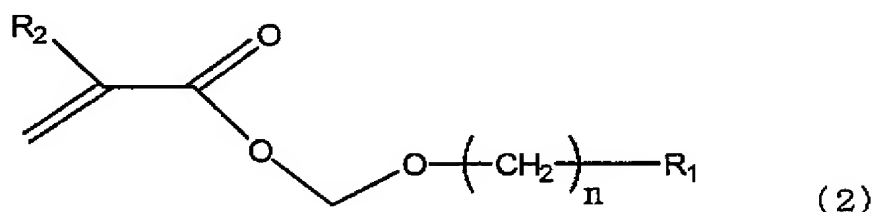
It is preferable that  $R_1$  in the general formula (1) represent a cycloaliphatic group which contains no more than 20 carbon atoms, and contains an adamantane backbone. Moreover, it is preferable that  $R_1$  represent a cycloaliphatic group containing at least one hydrophilic group, and that the hydrophilic group be at least one selected from the group consisting of a carbonyl group, an ester group, an alcoholic hydroxyl group, ether, an imino group, and an amino group.

[0015]

A novel compound of the present invention is represented by a general formula (2):

15 [0016]

[Chem 2]



[0017]

(wherein  $R_1$  and  $n$  represent the same as the aforementioned; and  $R_2$  represents a hydrogen atom, a fluorine atom, a lower alkyl group containing 1 to 20 carbon atoms, or a fluorinated lower alkyl group containing 1 to 20 carbon atoms.), and a polymer compound containing a structural unit (a1) derived from the compound represented by the general formula (2) is included in a polymer compound of the present invention.

[0018]

25 A photoresist composition of the present invention includes a base material resin

component (A) (hereinafter, may be referred to as a “component (A)”.) which exhibits changed alkali solubility under the action of an acid; and an acid generator component (B) (hereinafter, may be referred to as a “component (B)”.) which generates the acid on exposure to radiation, wherein the base material resin component (A) is a polymer compound of the present invention.

[0019]

A resist pattern formation method of the present invention includes forming a photoresist film on a substrate using a photoresist composition of the present invention; exposing the photoresist film; and developing the photoresist film to form a resist pattern.

[Effect of the Invention]

[0020]

According to the present invention, it is possible to provide a fine pattern with high resolution and a favorable resist pattern shape (rectangularity). Also, an acid dissociable, dissolution inhibiting group can be dissociated by even an acid generator generating an acid whose acid strength is weak, and it is possible to obtain favorable sensitivity.

[Best Mode for Carrying out the Invention]

[0021]

A detailed description of the present invention is as follows.

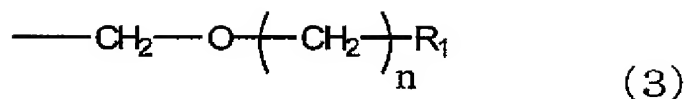
In the present claims and specification, a “structural unit” means a monomer unit constituting a polymer compound.

In the present claims and specification, an alkyl group, an alkoxy group, or an alkylene group may be linear or branched unless otherwise noted.

In a polymer compound of present invention, at least one at least one hydrogen atom of an alkali soluble group (i) in this molecule is substituted by an acid dissociable, dissolution inhibiting group (ii) represented by a general formula (3):

[0022]

[Chem 3]



[0023]

(wherein R<sub>1</sub> represents a cycloaliphatic group which contains no more than 20 carbon atoms, and n represents 0 or an integer of 1 to 5.).

5 When a polymer compound of the present invention is used in the system of a chemically amplified positive resist, a dissolution inhibiting effect in an alkali developing solution is shown before exposure, whereas alkali solubility due to deprotection is shown after exposure and a PEB (post exposure baking) process because the polymer compound contains an acid dissociable, dissolution inhibiting group containing a cycloaliphatic  
10 group represented by the aforementioned general formula (1) or (3).

Since the alkali solubility is greatly changed before and after exposure, it is possible to provide a fine pattern excellent in resolution. Also, a polymer compound of the present invention improves etching resistance. In particular, when a hydrophilic group is further introduced into an acid dissociable, dissolution inhibiting group (ii), the  
15 adhesion of a resist pattern to a substrate is improved, and the affinity of a resist pattern to an alkali developing solution is improved, thereby reducing the developing defects. Also, mask linearity becomes favorable.

[0024]

[Acid dissociable, dissolution inhibiting group (ii)]

20 An alkali soluble group (i) is described below in detail. An alkali soluble group (i) contains a hydrogen atom which is substituted by an acid dissociable, dissolution inhibiting group (ii). In other words, when an alkali soluble group (i) is an alcoholic hydroxyl group, a carboxyl group, or a phenolic hydroxyl group, an acid dissociable,



dissolution inhibiting group (ii) is bonded to the oxygen atom of the alkali soluble group (i) in which one hydrogen atom has been removed.

[0025]

5 The acid dissociable, dissolution inhibiting group (ii) is represented by the general formula (1). In the general formula (1),  $R_1$  represents a cycloaliphatic group which contains no more than 20 carbon atoms, preferably a cycloaliphatic group which contains 5 to 12 carbon atoms. The cycloaliphatic group may contain a substituent group. A value of  $n$  is preferably 0 or 1.

10 The word "aliphatic" in the present claims and specification is defined as a relative conception to the word "aromatic", which means a non-aromatic group or compound. A "cycloaliphatic group" means a non-aromatic monocyclic group or polycyclic group (alicyclic group). A "cycloaliphatic group" is not limited to a group composed of carbon and hydrogen, although a hydrocarbon group is preferable. Also, a "hydrocarbon" can be saturated or unsaturated although it is usually preferable that a  
15 "hydrocarbon" be saturated.

Examples of the cycloaliphatic group include a monovalent group derived from cyclohexane, cyclopentane, adamantane, norbornane, norbornene, methylnorbornane, ethylnorbornane, methylnorbornene, ethylnorbornene, isobornane, tricyclodecane, or tetracyclododecane. The cycloaliphatic group can be appropriately selected to be used  
20 from among many cycloaliphatic groups having been proposed in an ArF resist. Among them, a cyclohexyl group, a cyclopentyl group, an adamantyl group, a norbornyl group, a norbornenyl group, a methylnorbornyl group, an ethylnorbornyl group, a methylnorbornenyl group, an ethylnorbornenyl group, or a tetracyclododecanyl group is industrially preferable, and an adamantyl group is most preferable.

25 [0026]

It is more preferable that  $R_1$  in the general formula (1), which represents the acid dissociable, dissolution inhibiting group (ii), represent a cycloaliphatic group containing at least one hydrophilic group. It is preferable that the hydrophilic group be a carbonyl group (preferably a ketonic carbonyl group), an ester group (-COOR), an

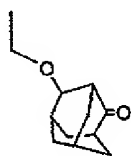
alcoholic hydroxyl group, ether (-OR), an imino group, and an amino group, and a carbonyl group is most preferable because it is easily available.

[0027]

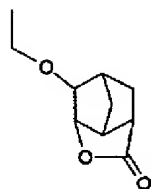
Examples of the acid dissociable, dissolution inhibiting group (ii) include the groups represented by the following chemical formulae (4) to (15).

[0028]

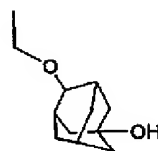
[Chem 4]



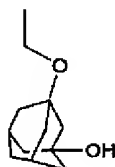
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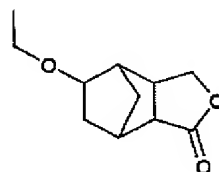
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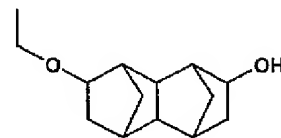
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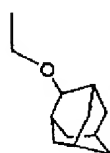
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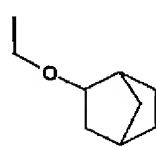
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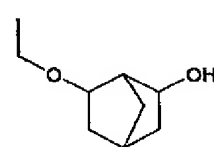
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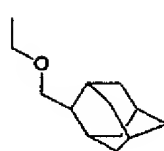
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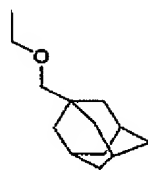
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[0029]

[Alkali soluble group (i)]

An alkali soluble group (i) in a polymer compound of the present invention is

known because examples are cited in the aforementioned non-patent references, and a KrF resist, an ArF resist, and an F<sub>2</sub> resist have been proposed. Examples of the alkali soluble group (i) include an alcoholic hydroxyl group, a phenolic hydroxyl group, and a carboxyl group, and there is no limitation to these groups.

5 In the present invention, it is preferable that the alkali soluble group be at least one selected from an alcoholic hydroxyl group, a phenolic hydroxyl group, or a carboxyl group. Among them, an alcoholic hydroxyl group is preferable because it has high transparency and appropriate alkali solubility. Also, among alcoholic groups, it is more preferable that a carbon atom adjacent to the carbon atom bonded to the alcoholic  
10 hydroxyl group be bonded to at least one fluorine atom.

[0030]

The alcoholic hydroxyl group can be a simple hydroxyl group, an alcoholic hydroxyl group-containing alkyloxy group, an alcoholic hydroxyl group-containing alkyloxyalkyl group, or an alcoholic hydroxyl group-containing alkyl group. Examples  
15 of an alkyloxy group, an alkyloxyalkyl group, and an alkyl group include a lower alkyloxy group, a lower alkyloxy-lower alkyl group, and a lower alkyl group, respectively. Herein, the word "lower" represents no more than 4 carbon atoms.

[0031]

Specific examples of the lower alkyloxy group include a methyloxy group, an  
20 ethyloxy group, a propyloxy group, and a butyloxy group. Specific examples of the lower alkyloxy-lower alkyl group include a methyloxymethyl group, an ethyloxymethyl group, a propyloxymethyl group, and a butyloxymethyl group. Specific examples of the lower alkyl group include a methyl group, an ethyl group, a propyl group, and a butyl group.

25 [0032]

Also, at least one or all of the hydrogen atoms of an alkyloxy, alkyloxyalkyl, or alkyl group in the aforementioned alcoholic hydroxyl group-containing alkyloxy, alcoholic hydroxyl group-containing alkyloxyalkyl, or alcoholic hydroxyl group-containing alkyl group may be substituted by a fluorine atom. Preferable examples

include an alcoholic hydroxyl group-containing alkyloxy group in which at least one of the hydrogen atoms of an alkyloxy part is substituted by a fluorine atom, an alcoholic hydroxyl group-containing alkyloxyalkyl group in which at least one of the hydrogen atoms of an alkyloxy part is substituted by a fluorine atom, and an alcoholic hydroxyl group-containing alkyl group in which at least one of the hydrogen atoms of an alkyl group is substituted by a fluorine atom. In other words, preferable examples include an alcoholic hydroxyl group-containing fluoroalkyloxy group, an alcoholic hydroxyl group-containing fluoroalkyloxyalkyl group, or an alcoholic hydroxyl group-containing fluoroalkyl group.

10 [0033]

Examples of the alcoholic hydroxyl group-containing fluoroalkyloxy group include a 2-bis(trifluoromethyl)-2-hydroxy-ethyloxy group (  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{O}-$  ) and a 3-bis(trifluoromethyl)-3-hydroxypropyloxy group (  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{CH}_2\text{O}-$  ).

Examples of the alcoholic hydroxyl group-containing fluoroalkyloxyalkyl group include a  
 15  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{O}-\text{CH}_2-$  group and a  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2-$  group. Examples of the alcoholic hydroxyl group-containing fluoroalkyl group include a 2-bis(trifluoromethyl)-2-hydroxy-ethyl group (  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2-$  ) and a 3-bis(trifluoromethyl)-3-hydroxypropyl group (  $(\text{HO})\text{C}(\text{CF}_3)_2\text{CH}_2\text{CH}_2-$  ).

[0034]

20 Examples of the phenolic hydroxyl group include phenolic hydroxyl groups of a novolak resin and poly-( $\alpha$ -methyl)hydroxystyrene. Among them, a phenolic hydroxyl group of poly-( $\alpha$ -methyl)hydroxystyrene is preferable because it is inexpensive and easily available.

[0035]

25 Examples of the carboxyl group include a carboxyl group of a structural unit derived from an ethylenic unsaturated carboxylic acid. Examples of this ethylenic unsaturated carboxylic acid include an unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic acid, or fumaric acid. Among them, acrylic acid and methacrylic acid are preferable because they are inexpensive and easily available.

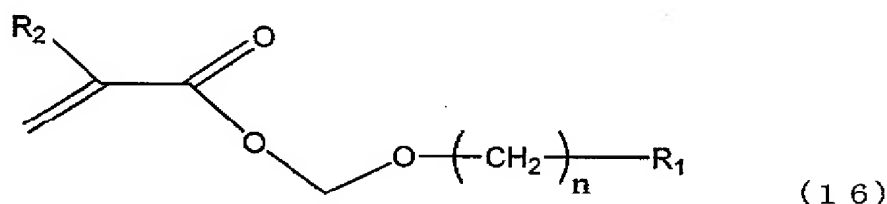
[0036]

[Compound of the present invention and structural unit (a1)]

A novel compound of the present invention (may be referred to as a “low molecular weight compound” in comparison with a polymer compound of the present invention) is represented by a following general formula (16):

[0037]

[Chem 5]



10 [0038]

(wherein  $\text{R}_2$  represents a hydrogen atom, a fluorine atom, a lower alkyl group containing no more than 20 carbon atoms, or a fluorinated lower alkyl group containing no more than 20 carbon atoms;  $\text{R}_1$  represents a cycloaliphatic group which contains no more than 20 carbon atoms; and  $n$  represents 0 or an integer of 1 to 5.). Also, a polymer compound containing a structural unit (a1) derived from the compound as a monomer unit is included in a polymer compound of the present invention.

The structural unit (a1) corresponds to a structural unit derived from a novel compound of the present invention in which the alkali soluble group (i) is a carboxyl group derived from acrylic acid which may contain a substituent group ( $\text{R}_2$ ), and a hydrogen atom of the carboxyl group is substituted by an acid dissociable, dissolution inhibiting group (ii).

[0039]

In the general formula (16),  $\text{R}_2$  represents a hydrogen atom, a fluorine atom, a lower alkyl group containing no more than 20 carbon atoms, or a fluorinated lower alkyl group containing no more than 20 carbon atoms; preferably a lower alkyl group

containing 1 to 4 carbon atoms or a fluorinated lower alkyl group containing 1 to 4 carbon atoms, and examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, and trifluoromethyl group. Among them, a hydrogen atom and a methyl group are most preferable because they are inexpensive and easily available. A value of

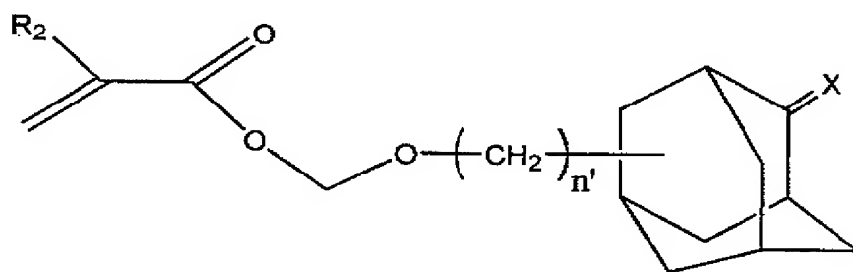
5 n is 0 or an integer of 1 to 5, preferably 0 or 1.

[0040]

Preferable examples of a compound represented by the general formula (16) include a compound represented by a following general formula (17):

[0041]

10 [Chem 6]



(17)

[0042]

(wherein  $R_2$  represents the same as the aforementioned, X represents two hydrogen atoms or an oxygen atom, and  $n'$  represents 0 or 1.).

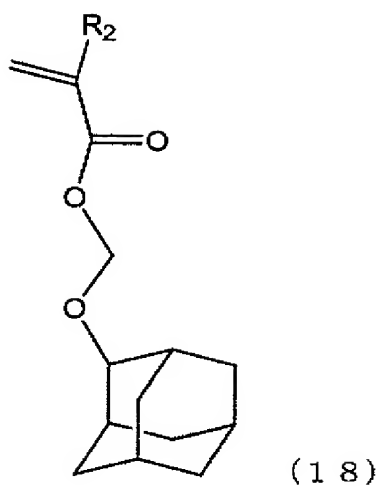
15 In other words, when X represents two hydrogen atoms, a methylene chain ( $-CH_2-$ ) is formed.

[0043]

Among compounds represented by the general formula (17), more preferable examples include compounds represented by the following general formulae (18) to (20).

20 [0044]

[Chem 7]



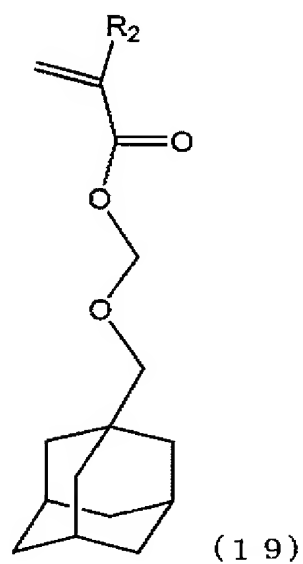
[0045]

(wherein R<sub>2</sub> represents the same as the aforementioned.)

[0046]

5

[Chem 8]



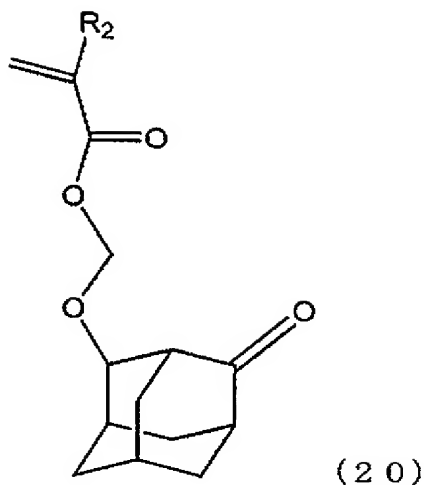
[0047]

(wherein R<sub>2</sub> represents the same as the aforementioned.)

[0048]

10

[Chem 9]



[0049]

(wherein  $R_2$  represents the same as the aforementioned.)

[0050]

5 [Polymer compound]

The polystyrene equivalent weight average molecular weight ( $M_w$ ) determined using gel permeation chromatography (GPC) of a polymer compound of the present invention is preferably 5,000 to 80,000, more preferably 8,000 to 50,000 for use in a photoresist composition, although there is no limitation to these ranges. Also, the degree  
 10 of dispersion ( $M_w / M_n$ ) is about 1.0 to 5.0, preferably no more than 2.5.  $M_n$  is a number average molecular weight.

[0051]

A precursor of a polymer compound of the present invention before introducing an acid dissociable, dissolution inhibiting group (ii) can be composed of one, or two or  
 15 more structural units containing an alkali soluble group (i). Hereinafter, as a matter of convenience of explanation, a "precursor" or a "polymer compound" may be referred to as a polymer compound before or after introducing an acid dissociable, dissolution inhibiting group (ii), respectively, so as to distinguish both.

One, or two or more structural units selected from monomer units including the



alcoholic hydroxyl group, the phenolic hydroxyl group, and the carboxyl group are used as a structural unit including the alkali soluble group. In addition to those, a structural unit including the alkali soluble group (i) can further include a structural unit used in a conventional polymer compound for a photoresist composition.

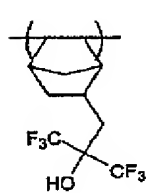
5 [0052]

Examples of a structural unit including the alkali soluble group include structural units containing the alcoholic hydroxyl groups in which a carbon atom adjacent to the carbon atom bonded to the alcoholic hydroxyl group is bonded to at least one fluorine atom as represented by the following chemical formulae (21) to (29); structural  
10 units containing a phenolic hydroxyl group as represented by the following chemical formulae (30) to (31); and structural units containing a carboxyl group as represented by the following chemical formulae (32) to (35) and (45) in which  $R^7$  represents a hydrogen atom.

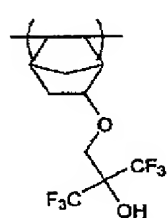
Herein, it is preferable that the structural unit represented by the chemical  
15 formula (22) be used in combination with a structural unit derived from tetrafluorinated ethylene as represented by the chemical formula (23).

[0053]

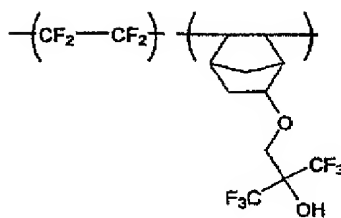
[Chem 10]



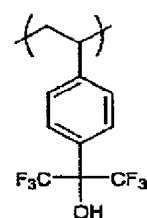
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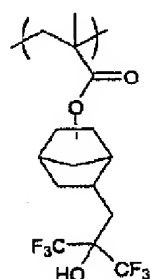
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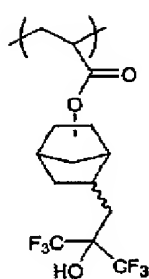
(23)



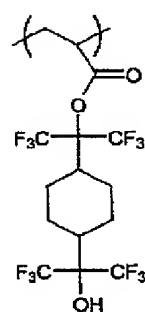
(24)



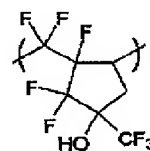
(25)



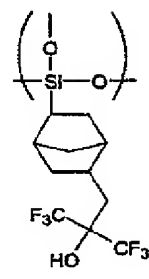
(26)



(27)



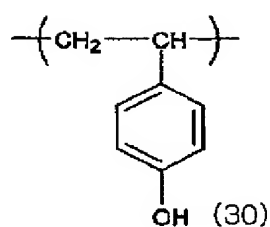
(28)



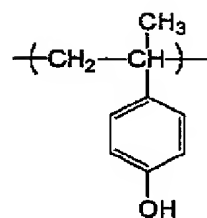
(29)

[0054]

[Chem 11]



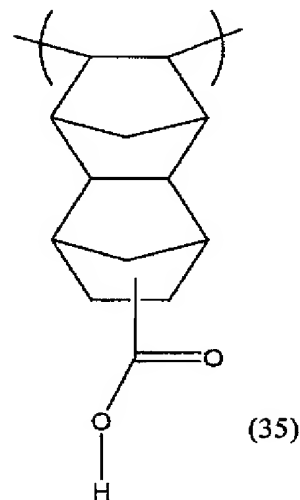
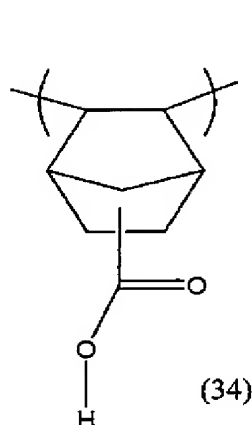
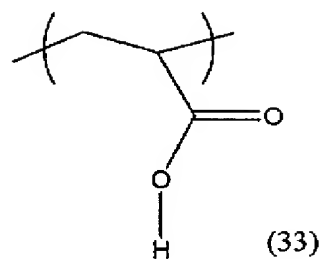
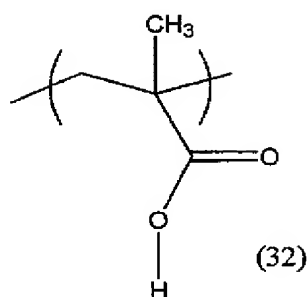
(30)



(31)

[0055]

[Chem 12]



[0056]

The polymer compound is synthesized by a known method or methods disclosed in the non-patent references.

- 5        Examples of a method for introducing an acid dissociable, dissolution inhibiting group (ii) by replacing a hydrogen atom of an alkali soluble group (i) in a precursor include a following method: synthesizing a halogenated methylether compound by using an alcohol compound containing a halogen atom such as chlorine or bromine; and reacting this halogenated methylether compound with an alkali soluble group (i) in a
- 10       precursor so as to introduce an acid dissociable, dissolution inhibiting group (ii). A detailed method is as follows: reacting a chloromethylether compound, which is a starting material, with any one alkali soluble group (i) selected from an alcoholic hydroxyl group, a carboxyl group, or a phenolic hydroxyl group in a precursor. Thus, the alkali soluble group (i) can be protected by an acid dissociable, dissolution inhibiting group (ii)
- 15       represented by the general formula (1).

[0057]

The chloromethylether compound can be synthesized by a known method represented by the following reaction formula. In other words, the desired chloromethylether compound can be obtained as follows: adding paraformaldehyde to an alcohol compound; injecting a hydrogen chloride gas at 2.0 to 3.0 equivalent amount per this alcohol compound; conducting the reaction at a temperature of 40°C to 100°C under acid conditions due to hydrochloric acid; and conducting distillation under reduced pressure of the product after completion of the reaction. In the following reaction formula, R corresponds to a group represented by “-(CH<sub>2</sub>)<sub>n</sub>-R<sub>1</sub>” in a desired compound.

[0058]

[Chem 13]

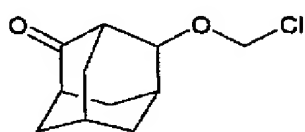


[0059]

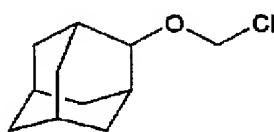
Examples of the chloromethylether compound include 4-oxo-2-adamantyl chloromethyl ether represented by the following chemical formula (36), 2-adamantyl chloromethyl ether represented by the following chemical formula (37), and 1-adamantyl chloromethyl ether represented by the following chemical formula (38).

[0060]

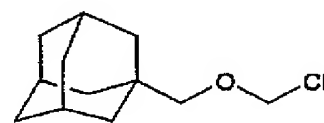
[Chem 14]



(36)



(37)



(38)

[0061]

A precursor containing a phenolic hydroxyl group as an alkali soluble group (i), can be obtained by reacting a poly-(α-methyl)hydroxystyrene resin with the halogenated methylether compound, for example.

[0062]

A precursor containing a carboxyl group as an alkali soluble group (i), can be obtained by the following method, for example: reacting the halogenated methylether compound with an unsaturated carboxylic acid such as acrylic acid or methacrylic acid; and polymerizing the obtained unsaturated carboxylate.

[0063]

An acid dissociable, dissolution inhibiting group (ii) can be introduced into an alkali soluble group (i) by reacting the halogenated methylether compound or another compound containing a cycloaliphatic group with a structural unit containing an alkali soluble group (i) represented by the chemical formulae (21) to (35) or a compound from which this structural unit is derived. Furthermore, a polymer compound of the present invention can be obtained by polymerizing the obtained structural units or compounds from which the structural units are derived, if necessary.

[0064]

Also, a novel compound (low molecular weight compound) of the present invention can be produced by reacting acrylic acid, which may contain a substituent group ( $R_2$ ), with the halogenated methylether compound. The introduction of a substituent group ( $R_2$ ) can be performed by an optional process.

[0065]

[Photoresist composition]

A photoresist composition of the present invention includes at least a base material resin component (A) which exhibits changed alkali solubility under the action of an acid; and an acid generator component (B) which generates the acid on exposure to radiation. Furthermore, the base material resin component (A) is the aforementioned polymer compound of the present invention.

[0066]

A photoresist composition of the present invention can be positive or negative as far as it includes the above characteristics.

In the case of a negative photoresist composition, an alkali soluble resin is used

as a component (A), and blended with a cross-linking agent. When an acid is generated from a component (B) on exposure during formation of a resist pattern, a cross-linkage occurs between an alkali soluble resin and the cross-linking agent under the action of the acid. Then, an alkali soluble resin is changed to be alkali insoluble. Examples of the cross-linking agent include an amino-type cross-linking agent such as a melamine containing a methylol group or an alkoxymethyl group, urea, or glycoluril.

In the case of a positive photoresist composition, a component (A) includes an alkali insoluble structural unit containing an acid dissociable, dissolution inhibiting group. An acid dissociable, dissolution inhibiting group is dissociated under the action of an acid which is generated from a component (B) on exposure. Then, a whole component (A) is changed from being alkali insoluble to being alkali soluble. Accordingly, when exposure through a mask pattern, or this exposure followed by post exposure baking (PEB) are performed during formation of a resist pattern, an exposed part is changed to alkali soluble, whereas an unexposed part remains alkali insoluble without change. Therefore, a positive resist pattern can be formed by alkali development. In the case of a positive photoresist composition, a polymer compound of the present invention is preferably used as a component (A).

[0067]

When a polymer compound containing a phenolic hydroxyl group as an alkali soluble group (i) is used as a precursor in the base material resin component (A), a ratio of a structural unit containing an alkali soluble group (i) to all structural units constituting the component (A) is preferably 50 to 95 mol%, more preferably 55 to 90 mol%. Meanwhile, the ratio of a structural unit protected by an acid dissociable, dissolution inhibiting group (ii) is preferably 3 to 50 mol%, more preferably 7 to 30 mol%.

[0068]

When a polymer compound containing an alcoholic hydroxyl group as an alkali soluble group (i) is used as a precursor in the base material resin component (A), a ratio of a structural unit containing an alkali soluble group (i) to all structural units constituting the component (A) is preferably 50 to 95 mol%, more preferably 55 to 90 mol%.

Meanwhile, the ratio of a structural unit protected by an acid dissociable, dissolution inhibiting group (ii) is preferably 3 to 50 mol%, more preferably 5 to 35 mol%.

[0069]

[Structural unit (a1)]

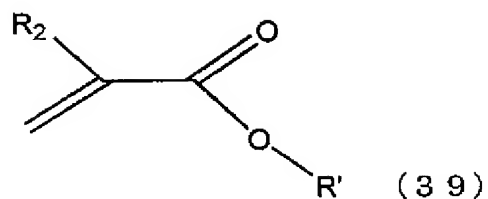
5        When a polymer compound containing a carboxyl group as an alkali soluble group (i) is used as a precursor in the base material resin component (A), it is preferable that a structural unit (a1) derived from a compound represented by the general formula (2) be used as a structural unit protected by an acid dissociable, dissolution inhibiting group (ii).

10        In this case, a polymer, which is obtained by copolymerizing the structural unit (a1) and other known structural units generally used in a chemically amplified photoresist composition, can be used as the base material resin component (A). Examples of the other structural units include the following structural units (a2) to (a6). For example, a structural unit forming a cyclic or linear tertiary alkylester with a carboxyl group of  
15        (meth)acrylic acid is well-known as the other structural unit.

      A structural unit derived from at least one compound selected from a following general formula (39) can be used as a structural unit (a1). Since these structural units contain an acetal group ( $-R-O-R'$ ; an alkoxyalkyl group), an acid dissociable, dissolution inhibiting group (ii) tends to be easily dissociated under the action of an acid in  
20        comparison with a structural unit (a2) described below, for example. Therefore, even an acid generator generating an acid whose acid strength is weak (such as a diazomethane-type acid generator, an oxime sulfonate-type acid generator, or an onium salt containing camphor sulfonic acid in an anion part, each being described below) can dissociate an acid dissociable, dissolution inhibiting group (ii) sufficiently.

25        [0070]

[Chem 15]



[0071]

(wherein R' represents a group represented by the chemical formulae (4) to (15), and R<sub>2</sub> represents the same as the aforementioned.)

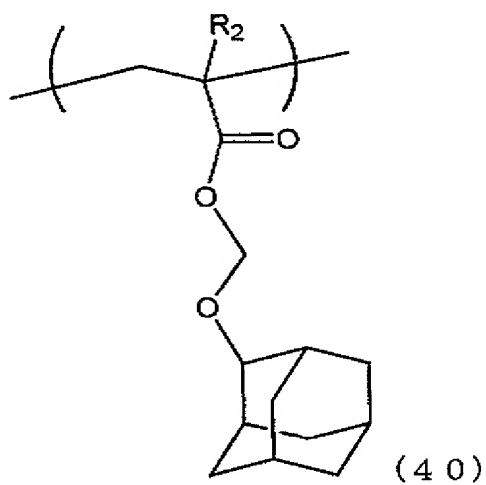
5

[0072]

Among them, it is preferable that a structural unit (a1) be at least one selected from structural units represented by the following chemical formulae (40) to (42).

[0073]

[Chem 16]



10

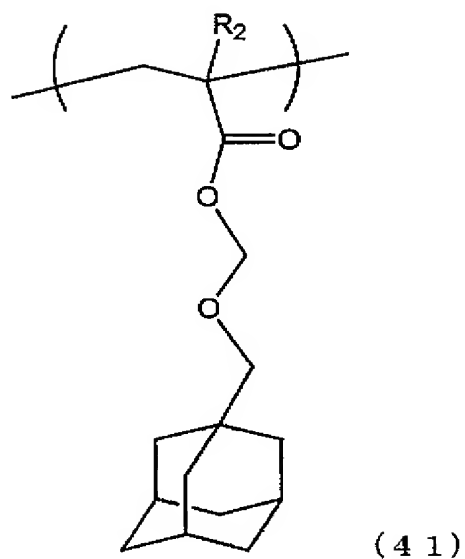
[0074]

(wherein R<sub>2</sub> represents the same as the aforementioned.)

[0075]

[Chem 17]





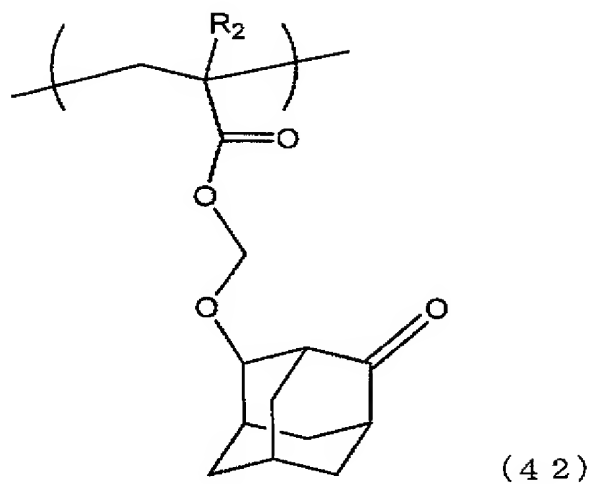
[0076]

(wherein  $R_2$  represents the same as the aforementioned.)

[0077]

5

[Chem 18]



[0078]

(wherein  $R_2$  represents the same as the aforementioned.)

[0079]

It is preferable that the line edge roughness is reduced by using a structural unit (a1) represented by any one of the chemical formulae (40) to (42) as a structural unit containing an acid dissociable, dissolution inhibiting group. Also, it is preferable that since even a weak acid can dissociate an acid dissociable, dissolution inhibiting group (ii),  
5 various acid generators can be used.

In addition, exposure margin is improved, and exposure area margin is also improved.

In addition, it is preferable that the thermal stability is improved because a  
10 structural unit (a1) shows a higher heat decomposition point than a tertiary ester compound of (meth)acrylic acid such as structural unit (a2) described below. Accordingly, storage stability is also improved. Moreover, it is possible to perform PEB at low temperature because a structural unit (a1) shows a lower Tg (glass transition point) than a structural unit (a2) described below and dissociates a protecting group during  
15 exposure (a structural unit (a2) dissociates a protecting group during PEB.). In other words, it is possible to easily control diffusion of an acid generator; therefore, it is possible to easily control a resist pattern shape. In addition, it is preferable that the PEB margin becomes favorable.

[0080]

20 A component (A) of a photoresist composition of the present invention can include a structural unit (a2) described below as a structural unit containing an acid dissociable, dissolution inhibiting group, although the ratio of the structural unit (a1) as an acid dissociable, dissolution inhibiting group in a component (A) is preferably 50% by mass or more, more preferably 80% by mass, and most preferably 100% by mass.

25 [0081]

[Structural unit (a2)]

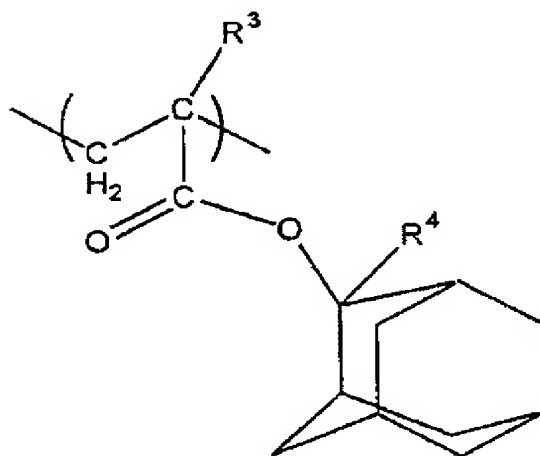
A structural unit (a2) is a structural unit derived from a (meth)acrylate containing a monocyclic or polycyclic group-containing acid dissociable, dissolution inhibiting group, and examples thereof include a structural unit containing an acid dissociable,

dissolution inhibiting group other than a structural unit (a1). These can be used in an amount range that does not deteriorate the effect of the present invention.

Examples of a monocyclic group include a group in which one hydrogen atom is removed from a cycloalkane, for example an aliphatic monocyclic group such as a cyclohexyl group or a cyclopentyl group. Examples of a polycyclic group include a group in which one hydrogen atom is removed from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane, or tetracyclododecane which is a bicycloalkane, a tricycloalkane, or a tetracycloalkane. In other words, an aliphatic polycyclic group can be cited. Herein, these monocyclic or polycyclic groups have been proposed in an ArF resist. In the present invention, it is possible to optionally select and use one from these monocyclic or polycyclic groups. Among them, an aliphatic polycyclic group such as an adamantyl group, a norbornyl group, or a tetracyclododecanyl group is preferable because they are easily available industrially. In detail, at least one structural unit selected from the following general formula (43), (44), or (45) is preferable because they are excellent in resolution, dry etching resistance, and so on.

[0082]

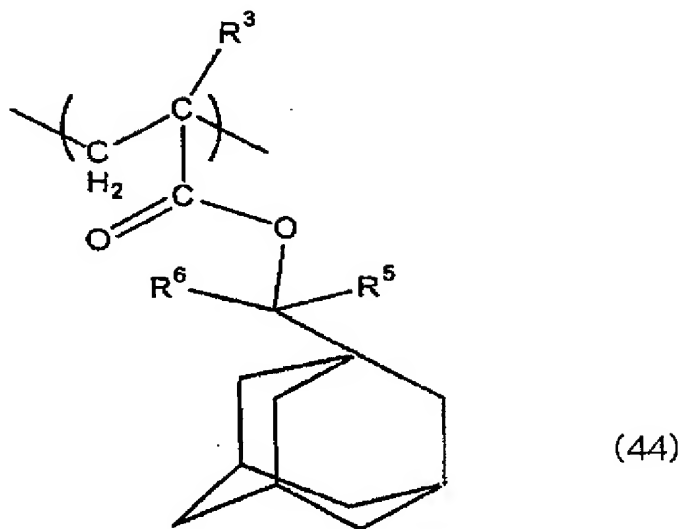
[Chem 19]



(43)

(wherein R<sup>3</sup> represents a hydrogen atom or a lower alkyl group, and R<sup>4</sup> represents a lower alkyl group.)

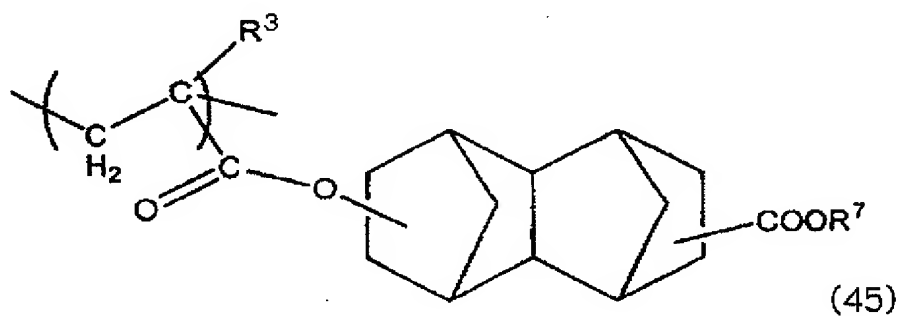
[Chem 20]



(wherein R<sup>3</sup> represents a hydrogen atom or a lower alkyl group, and R<sup>5</sup> and R<sup>6</sup> independently represents a lower alkyl group.)

10

[Chem 21]



[0087]

(wherein  $R^3$  represents a hydrogen atom or a lower alkyl group, and  $R^7$  represents a tertiary alkyl group.)

[0088]

In a structural unit represented by the general formula (43), a carbon atom  
5 adjacent to the oxygen atom (-O-) in an ester part of (meth)acrylic acid is a tertiary carbon in a ring backbone such as an adamantyl group which is a tertiary alkyl group.

Examples of  $R^3$  include a hydrogen atom, a methyl group, and a lower alkyl group containing about 2 to 5 carbon atoms, specifically a linear or branched, lower alkyl group such as an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an  
10 isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, or a neopentyl group.

Also, examples of  $R^4$  include a linear or branched, lower alkyl group such as a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, or a neopentyl  
15 group. Herein, it is preferable that  $R^4$  represent an alkyl group containing no less than 2 carbon atoms because they tend to have a higher acid dissociability than a methyl group. However, a methyl group and an ethyl group are most preferable industrially.

[0089]

In a structural unit represented by a general formula (44), a carbon atom adjacent  
20 to the oxygen atom (-O-) in an ester part of (meth)acrylic acid is a tertiary carbon in a tertiary alkyl group in which a ring backbone such as an adamantyl group exists.  $R^3$  represents the same as in the general formula (43), and  $R^5$  and  $R^6$  independently represents a lower alkyl group that is the aforementioned linear or branched alkyl group containing about 1 to 5 carbon atoms. These groups tend to have a higher acid  
25 dissociability than a 2-methyl-2-adamantyl group. Herein, it is industrially preferable that both of  $R^5$  and  $R^6$  represent a methyl group.

[0090]

In a structural unit represented by a general formula (45), a carbon atom adjacent to the oxygen atom (-O-) in another ester part than the ester part of (meth)acrylic acid is a

tertiary carbon in a tertiary alkyl group, and the other ester part and the ester part of (meth)acrylic acid is linked through a ring backbone such as a tetracyclododecanyl group. In a structural unit represented by the general formula (45),  $R^3$  represents the same as in the general formula (43),  $R^7$  represents a tertiary alkyl group such as a tert-butyl group or a tert-amyl group. Herein, it is industrially preferable that  $R^7$  represent a tert-butyl group.

Also, among these structural units represented by the general formulae (43) to (45), the structural unit represented by the general formulae (43), in which  $R^4$  represents a methyl group or an ethyl group, is preferable because it is excellent in resolution.

10 [0091]

[Structural unit (a3)]

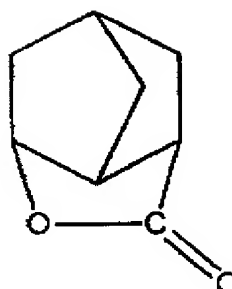
A structural unit (a3) is a structural unit derived from (meth)acrylate containing a lactone-containing monocyclic or polycyclic group. A lactone functional group is useful for improving the following characteristics of a photoresist film formed of a photoresist composition of the present invention: the adhesion to a substrate and the affinity to a developing solution.

Herein, a lactone ring means one ring containing a structure of  $-O-C(O)-$ , and the ring is counted as a first ring. Accordingly, a group containing only a lactone ring is referred to as a monocyclic group and a group containing other cyclic structures in addition to a lactone ring is referred to as a polycyclic group regardless of their structures.

As a structural unit (a3), any structural unit can be used without any particular limitation as long as it contains both a lactone functional group and a cyclic group. In detail, examples of a lactone-containing monocyclic group include a group in which one hydrogen atom is removed from  $\gamma$ -butyrolactone, and examples of a lactone-containing polycyclic group include a group in which one hydrogen atom is removed from a bicycloalkane, a tricycloalkane, or a tetracycloalkane, each containing a lactone group. In particular, a group in which one hydrogen atom is removed from a lactone-containing tricycloalkane represented by the following structural formula (46) or (47) is preferable because it is easily available industrially.

[0092]

[Chem 22]

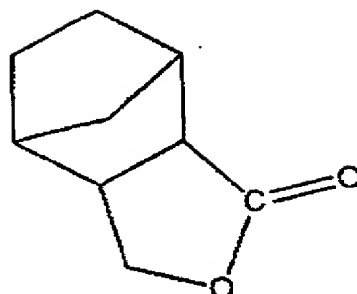


(46)

[0093]

5

[Chem 23]



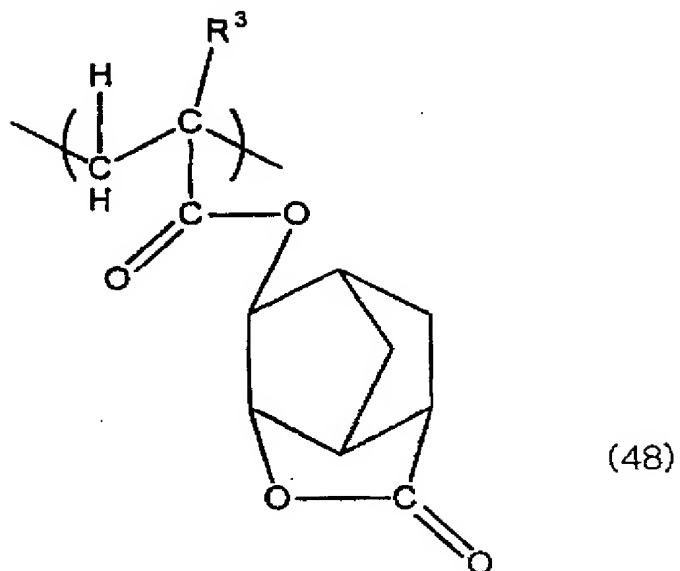
(47)

[0094]

Also, specific examples of a structural unit (a3) include a structural unit derived from (meth)acrylate containing a lactone-containing monocycloalkyl or tricycloalkyl group, and more specific examples include a structural unit represented by the following general formulae (48) to (50).

[0095]

[Chem 24]



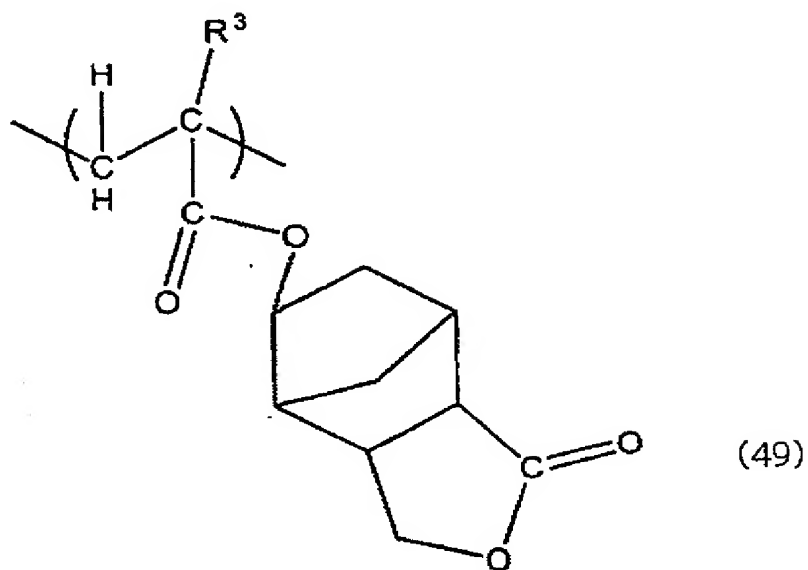
[0096]

(wherein R<sup>3</sup> represents a hydrogen atom or a lower alkyl group.)

[0097]

5

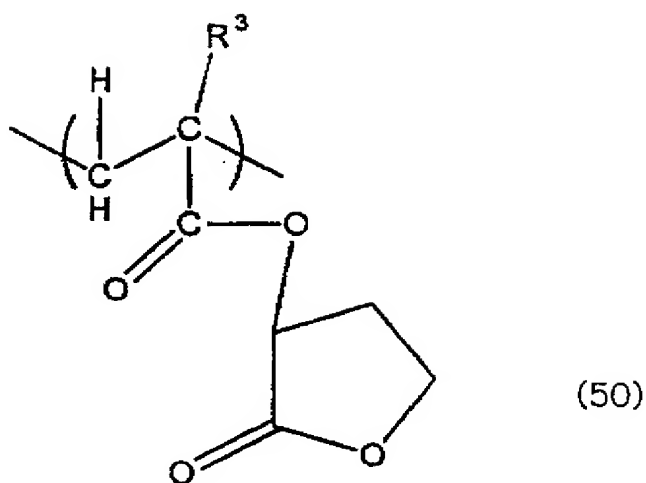
[Chem 25]

(wherein R<sup>3</sup> represents a hydrogen atom or a lower alkyl group.)

[0098]



[Chem 26]



[0099]

(wherein  $R^3$  represents a hydrogen atom or a lower alkyl group.)

5 [0100]

Examples of  $R^3$  include a hydrogen atom, a methyl group, and a lower alkyl group containing about 2 to 5 carbon atoms, specifically a linear or branched, lower alkyl group such as an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, or a neopentyl group.

10 [0101]

Among these structural units represented by general formulae (48) to (50), a structural unit derived from  $\gamma$ -butyrolactone ester of (meth)acrylic acid containing an ester bond at  $\alpha$ -carbon, namely (meth)acrylate of  $\gamma$ -butyrolactone, as represented by the general formula (50) is preferable because it is excellent in the inhibition and reduction effects against a proximity effect.

Also, a structural unit derived from norbornane-lactone ester of (meth)acrylic acid, namely (meth)acrylate of norbornane-lactone, as represented by the general formula (48) or (49) is preferable because it has a favorable shape of an obtained resist pattern, for example rectangularity. In particular, a structural unit represented by the formula (49) is

20

preferable because the above effect is quite high.

[0102]

The structural unit (a3) can be used alone or in combination of two or more being different from each other. It is preferable that the adhesion to a substrate, the affinity to an alkali developing solution, and the etching resistance of a photoresist film are further improved by introducing two or more lactone backbones being different from each other into a resin backbone. Preferable examples of the combination of lactones include a combination of a monocyclic lactone and a polycyclic lactone. Also, a combination of a structural unit derived from (meth)acrylate of  $\gamma$ -butyrolactone as represented by the general formula (50) and a structural unit derived from (meth)acrylate of norbornane-lactone as represented by the general formula (48) or (49) is most preferable because etching resistance and adhesion to a substrate are improved.

[0103]

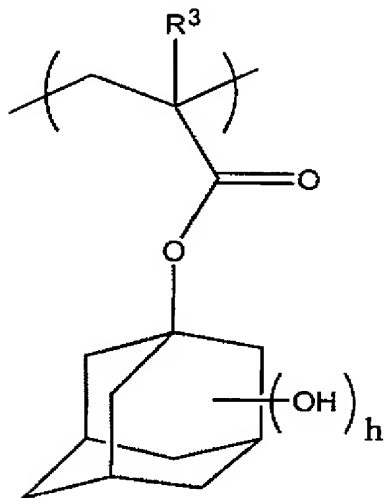
[Structural unit (a4)]

A structural unit (a4) is a structural unit derived from (meth)acrylate containing a polar group-containing polycyclic group. By containing a polar group, a structural unit (a4) can improve the affinity of all the resin component (A) to an alkali developing solution and the alkali solubility in an exposed part, thereby contributing to improving resolution. Herein, as a polycyclic group, the same polycyclic group can be used as in the structural unit (a1). Examples of the polar group include a cyano group, a carboxyl group, and a hydroxyl group, and a hydroxyl group is preferable.

As a structural unit (a4), any structural unit can be used without any particular limitation, as long as it contains a polar group-containing polycyclic group. In detail, a structural unit containing a hydroxyl group-containing adamantyl group, particularly a structural unit represented by a following general formula (51) is preferable because it possesses the effects of improving dry etching resistance and making a cross-sectional surface of a pattern rectangular.

[0104]

[Chem 27]



[0105]

(wherein  $R^3$  represents the same as the aforementioned,  $h$  represents an integer of 1 to 3.)

[0106]

Among them, a structural unit is preferable, in which  $h$  represents 1, and a hydroxyl group is bonded to the 3rd position of an adamantyl group.

[0107]

[Structural unit (a5)]

A structural unit (a5) is a structural unit derived from (meth)acrylate containing a polycyclic group-containing, non-acid dissociable, dissolution inhibiting group other than the structural units (a1) to (a4).

A structural unit derived from (meth)acrylate containing a polycyclic group-containing, non-acid dissociable, dissolution inhibiting group means a structural unit capable of enhancing the hydrophobicity of all the component (A) before and after exposure, thereby inhibiting alkali solubility. In other words, the structural unit (a5) is a structural unit containing a group which reduces alkali solubility of all the component (A) before exposure, which is not dissociated under the action of an acid generated from a component (B) after exposure, and which possesses a dissolution inhibiting property reducing alkali solubility of all the component (A) as long as it does not become alkali

insoluble when it is changed to alkali soluble by dissociating an acid dissociable, dissolution inhibiting group (ii) of the structural unit (a1) or (a2).

[0108]

5 The structural unit (a5) does not overlap the structural units (a1) to (a4). In other words, the structural unit (a5) does not contain any of an acid dissociable, dissolution inhibiting group (ii) in the structural units (a1) and (a2), a lactone group in the structural unit (a3), and a polar group in the structural unit (a4).

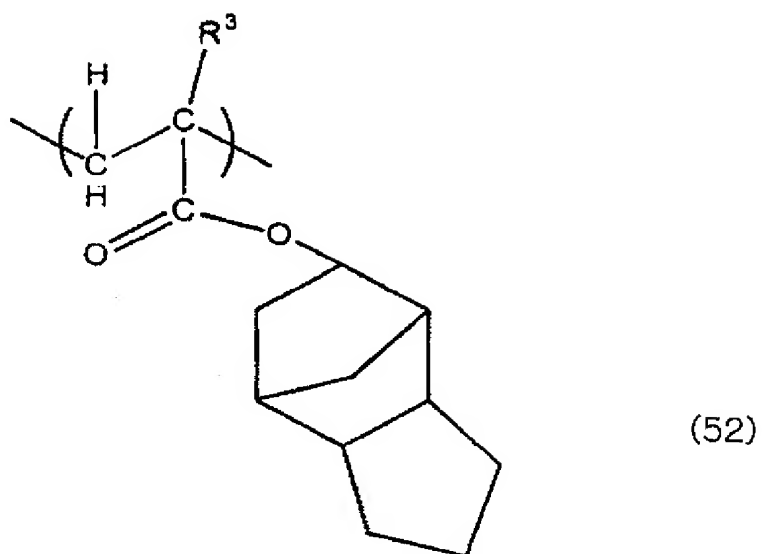
As a polycyclic group in the structural unit (a5), the same polycyclic group can be used as in the structural unit (a2).

10 [0109]

As a structural unit (a5), many structural units can be used, which are conventionally known as an ArF positive resist material. In particular, a structural unit derived from at least one selected from tricyclodecanyl (meth)acrylate, adamantyl (meth)acrylate, or tetracyclododecanyl (meth)acrylate because it is easily available  
15 industrially. These examples of a structural unit (a5) are represented by following general formulae (52) to (54). Among them, a structural unit represented by the general formula (52) is preferable because a shape of an obtained resist pattern such as rectangularity is particularly favorable.

[0110]

20 [Chem 28]



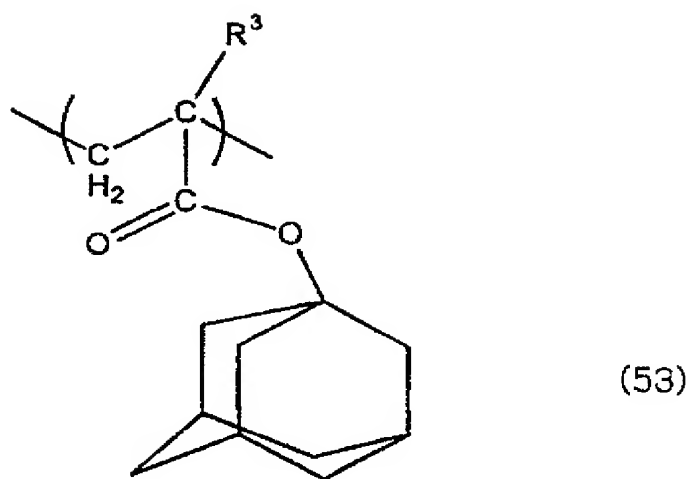
[0111]

(wherein R<sup>3</sup> represents a hydrogen atom or a lower alkyl group.)

[0112]

5

[Chem 29]



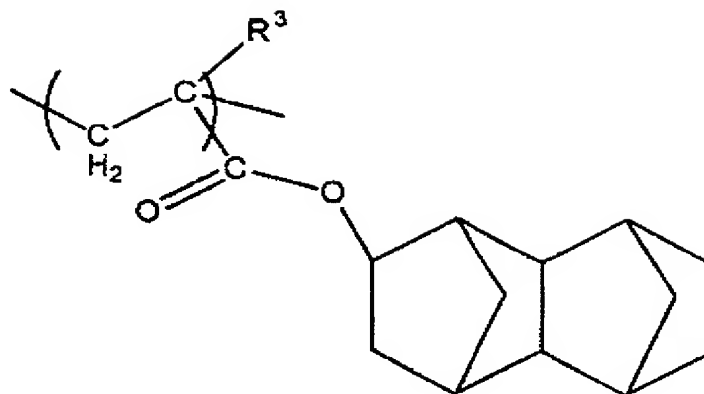
[0113]

(wherein R<sup>3</sup> represents a hydrogen atom or a lower alkyl group.)

[0114]

10

[Chem 30]



(54)

[0115]

(wherein  $R^3$  represents a hydrogen atom or a lower alkyl group.)

[0116]

5        Examples of  $R^3$  include a hydrogen atom, a methyl group, and a lower alkyl group containing about 2 to 5 carbon atoms, specifically a linear or branched, lower alkyl group such as an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, or a neopentyl group.

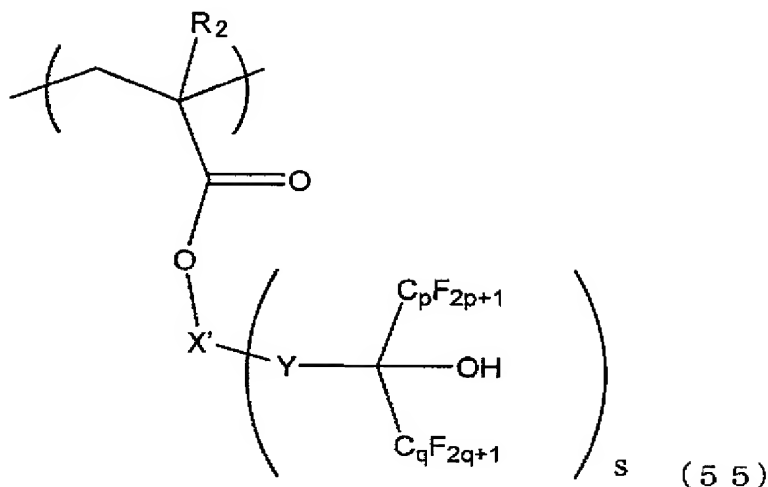
10        [0117]

[Structural unit (a6)]

A structural unit (a6) is a structural unit which does not overlap the structural units (a1) to (a5), which is represented by a following general formula (55), and which is derived from a compound containing a cyclic group X' bonded to acrylate which may  
 15        contain a substituent group and a fluorinated organic group bonded to the cyclic group X'. The fluorinated organic group is formed by replacing at least one hydrogen atom of an organic group with fluorine and contains an alcoholic hydroxyl group. When a base material resin component (A) includes the structural unit (a6), alkali solubility is improved. In addition, it is preferable that the resolution is improved due to the  
 20        enhancement of dissolution contrast.

[0118]

[Chem 31]



[0119]

$R_2$  represents the same as the aforementioned,  $X'$  represents a divalent or trivalent cyclic group,  $Y$  represents an alkylene or alkyloxy group containing 1 to 6 carbon atoms which is divalent,  $p$  and  $q$  independently represent an integer of 1 to 5, and  $s$  represents an integer of 1 or 2.

[0120]

In the general formula (55), as a divalent or trivalent cyclic group represented by  $X'$ , any group can be used without any particular limitation as long as it is a cyclic group, and examples thereof include aliphatic and aromatic cyclic groups. Among them, an aromatic cyclic group can be used in a photoresist composition for KrF exposure. In particular, it is preferable that an aliphatic cyclic group be used in a photoresist composition for ArF exposure because the transparency of a photoresist film is improved.

When  $X'$  is divalent,  $s$  represents 1. When  $X'$  is trivalent,  $s$  represents 2. In other words, when  $X'$  is trivalent, two fluorinated organic groups are bonded to  $X'$ .

[0121]

As an aromatic cyclic group, various aromatic monocyclic or polycyclic groups which are divalent or trivalent can be used without any particular limitation. Examples thereof include a group in which two or three hydrogen atoms are removed from an aromatic hydrocarbon, and examples of the aromatic hydrocarbon include benzene,

naphthalene, and anthracene.

[0122]

As an aliphatic cyclic group, various aliphatic monocyclic or polycyclic groups which are divalent or trivalent can be used without any particular limitation. Examples of the aliphatic cyclic group include a group in which two or three hydrogen atoms are removed from an aliphatic cyclic hydrocarbon, and examples of the aliphatic cyclic hydrocarbon include an aliphatic monocyclic hydrocarbon such as cyclohexane or cyclopentane and an aliphatic polycyclic hydrocarbon. The groups in which two or three hydrogen atoms are removed from these hydrocarbons can be used as an aliphatic cyclic group.

Among them, an aliphatic polycyclic hydrocarbon is more preferable, and examples thereof include adamantane, norbornane, norbornene, methylnorbornane, ethylnorbornane, methylnorbornene, ethylnorbornene, isobornane, tricyclodecane, or tetracyclododecane. The aliphatic polycyclic hydrocarbon can be appropriately selected and used from among many cycloaliphatic groups having been proposed in an ArF resist. Among them, adamantane, norbornane, norbornene, methylnorbornane, ethylnorbornane, methylnorbornene, ethylnorbornene, or tetracyclododecane is preferable industrially, and norbornane is most preferable.

Y represents an alkylene or alkyloxy group containing 1 to 6 carbon atoms which is divalent, and there is no particular limitation although a methylene group is preferable. It is preferable that each of p, q, and s represent 1.

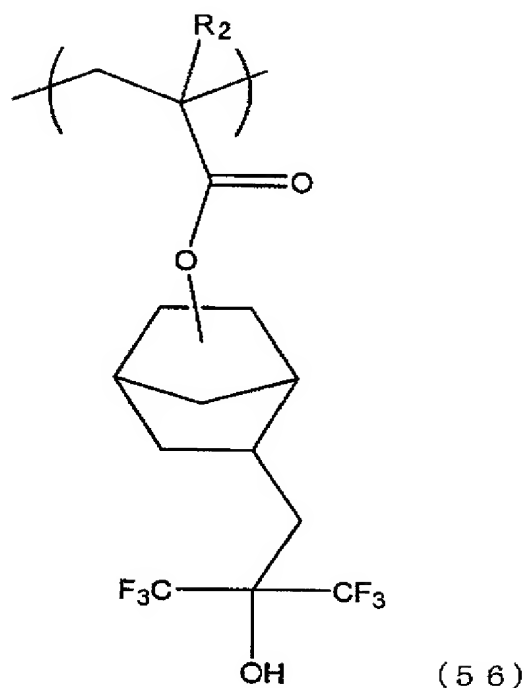
[0123]

Among them, a compound represented by a following general formula (56) is most preferable.

[0124]

[Chem 32]





[0125]

(wherein R<sub>2</sub> represents the same as the aforementioned.)

[0126]

5 [Other structural units]

Also, in a positive photoresist composition of the present invention, a copolymer can be used as the component (A), which is formed by appropriately combining structural units derived from: acrylic acid derivative or metacrylic acid derivative containing a dry etching resistance-enhancing group or non-acid dissociable, dissolution inhibiting group, which is known as a conventional, chemically amplified positive resist; carboxylic acid containing an ethylenic double bond for enhancing alkali solubility, such as acrylic acid, metacrylic acid, maleic acid, or fumaric acid; and a known monomer used for producing an acryl resin.

[0127]

15 Examples of the acrylic acid derivative include acrylate, in which a hydroxyl group of a carboxyl group is protected by a dry etching resistance-enhancing group or non-acid dissociable, dissolution inhibiting group, such as naphthyl acrylate, benzyl

acrylate, 3-oxocyclohexyl acrylate, an ester of acrylic acid and terpineol, or an ester of acrylic acid and 3-bromoacetone. Also, examples of the methacrylic acid derivative include a methacrylic acid derivative corresponding to the aforementioned acrylic acid derivative.

5 [0128]

Also, examples of the carboxylic acid containing an ethylenic double bond include acrylic acid, methacrylic acid, maleic acid, and fumaric acid.

Examples of a known monomer used for producing an acrylic resin include an alkyl acrylate such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate,  
10 n-butyl acrylate, isobutyl acrylate, n-hexyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, 2-hydroxyethyl acrylate, or 2-hydroxypropyl acrylate; and a methacrylate corresponding to the alkylacrylate.

[0129]

[Polymer compound including structural unit (a1)]

15 As a polymer compound which is preferable as the base material resin component (A) used in a positive resist composition of the present invention, a copolymer including structural units (a1) and (a3) is preferable because the resolution and the shape of a resist pattern become favorable. In particular, a polymer compound including structural units (a1), (a3), and (a4) is more preferable. Also, a polymer compound  
20 including two mutually different structural units (a3) in the base material resin is preferable.

[0130]

When a polymer compound of the present invention is used in a binary system (a copolymer of structural units (a1) and (a3)), the proportion of the structural unit (a1) is 20  
25 to 80 mol%, preferably 30 to 60 mol% per the sum of all structural units of the component (A), and the proportion of the structural unit (a3) is 20 to 80 mol%, preferably 30 to 60 mol%.

When a polymer compound of the present invention is used in a binary system (a copolymer of structural units (a1) and (a6)), the proportion of the structural unit (a1) is 20

to 80 mol%, preferably 30 to 60 mol% per the sum of all structural units of the component (A), and the proportion of the structural unit (a6) is 20 to 80 mol%, preferably 30 to 60 mol%. When a polymer compound of the present invention is used in a ternary system (a copolymer of structural units (a1), (a3), and (a4)), the proportion of the structural unit (a1) is 20 to 60 mol%, preferably 30 to 50 mol% per the sum of all structural units of the component (A), the proportion of the structural unit (a3) is 20 to 60 mol%, preferably 20 to 50 mol%, and the proportion of the structural unit (a4) is 10 to 50 mol%, preferably 20 to 40 mol%. When the proportions of all structural units in the component (A) are within the aforementioned ranges, it is preferable that the resolution and the dry etching resistance become excellent.

[0131]

When a polymer compound of the present invention is used in a quaternary system (a copolymer of structural units (a1), (a3), (a4), and (a5)), the proportion of the structural unit (a1) is 25 to 50 mol%, preferably 30 to 40 mol% per the sum of all structural units of the component (A), the proportion of the structural unit (a3) is 25 to 50 mol%, preferably 30 to 40 mol%, the proportion of the structural unit (a4) is 10 to 30 mol%, preferably 10 to 20 mol%, and the proportion of the structural unit (a5) is 3 to 25 mol%, preferably 5 to 20 mol%. When the proportions of all structural units in the component (A) are within the aforementioned ranges, it is possible to markedly improve depth of focus of an isolated pattern formed of an obtained positive resist composition and to sufficiently inhibit and reduce a proximity effect.

In addition, when the above-mentioned range is greatly exceeded, defects, such as poor-resolution, may arise. [0132]

The copolymers of structural units (a1) and (a3); structural units (a1) and (a6); structural units (a1), (a3), and (a4); structural units (a1), (a3), (a4), and (a5) can be copolymerized and used with a structural unit (a2) or other structural units in an amount range that does not deteriorate the effects of the present invention.

[0133]

The polymer compound including the structural unit (a1) can be obtained by

copolymerizing monomers, from which structural units are derived, according to a known radical polymerization method or the like using a radical polymerization initiator such as azobisisobutyronitrile (AIBN).

5 An amount of the base material component (A) in a photoresist composition of the present invention can be adjusted according to a desired thickness of a resist film to be formed. For example, this amount is adjusted to provide a preferable concentration of a solid part described below.

[0134]

[Component (B)]

10 A suitable acid generator component (B) used in a photoresist composition of the present invention can be selected from among known compounds which generate an acid on exposure to radiation. Examples of the acid generator (B) include an onium salt-type acid generator such as an iodonium salt or a sulfonium salt; an oxime sulfonate-type acid generator; a diazomethane-type acid generator such as bisalkyl- or bisaryl-  
15 sulfonyldiazomethanes, poly(bissulfonyl)diazomethanes, or diazomethanenitrobenzylsulfonates; an iminosulfonate-type acid generator; and a disulfonic acid-type acid generator.

[0135]

Specific examples of the onium salt-type acid generator include  
20 trifluoromethanesulfonate or nonafluorobutanesulfonate of diphenyliodonium; trifluoromethanesulfonate or nonafluorobutanesulfonate of bis(4-tert-butylphenyl)iodonium; trifluoromethanesulfonate, heptafluoropropanesulfonate, or nonafluorobutanesulfonate of triphenylsulfonium; trifluoromethanesulfonate, heptafluoropropanesulfonate, or nonafluorobutanesulfonate of tri(4-  
25 methylphenyl)sulfonium; trifluoromethanesulfonate, heptafluoropropanesulfonate, or nonafluorobutanesulfonate of dimethyl(4-hydroxynaphthyl)sulfonium; trifluoromethanesulfonate, heptafluoropropanesulfonate, or nonafluorobutanesulfonate of monophenyldimethylsulfonium; and trifluoromethanesulfonate, heptafluoropropanesulfonate, or nonafluorobutanesulfonate of

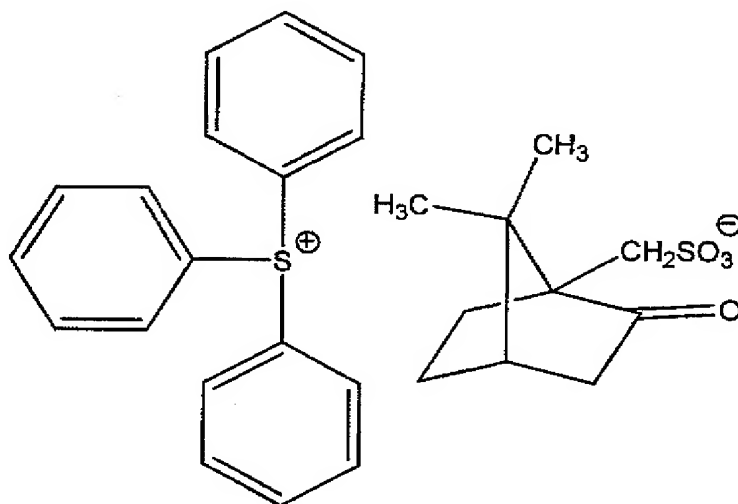
diphenylmonomethylsulfonium. Among them, an onium salt containing an anion of fluorinated alkyl sulfonic acid ion is preferable.

[0136]

Even an onium salt containing a camphor sulfonic acid ion in an anion part, whose acid strength is weak, can be used among the onium salt-type acid generators. Specific examples can include the compound represented by the following chemical formula (57).

[0137]

[Chem 33]



( 5 7 )

10

[0138]

Specific examples of the oxime sulfonate type acid generator include  $\alpha$ -(methylsulfonyloxyimino)-phenylacetonitrile,  $\alpha$ -(methylsulfonyloxyimino)-p-methoxyphenylacetonitrile,  $\alpha$ -(trifluoromethylsulfonyloxyimino)-phenylacetonitrile,  $\alpha$ -(trifluoromethylsulfonyloxyimino)-p-methoxyphenylacetonitrile,  $\alpha$ -(ethylsulfonyloxyimino)-p-methoxyphenylacetonitrile,  $\alpha$ -(propylsulfonyloxyimino)-p-methylphenylacetonitrile, and  $\alpha$ -(methylsulfonyloxyimino)-p-bromophenylacetonitrile. Among them  $\alpha$ -(methylsulfonyloxyimino)-p-methoxyphenylacetonitrile is preferable.

[0139]

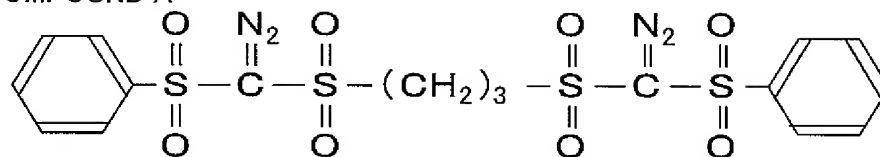
Specific examples of the bis(alkylsulfonyl)- or bis(arylsulfonyl)-diazomethanes of the diazomethane-type acid generator include bis(isopropylsulfonyl)diazomethane, bis(p-toluenesulfonyl)diazomethane, bis(1,1-dimethylethylsulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, bis(2,4-dimethylphenylsulfonyl)diazomethane.

- 5 Also, specific examples of the poly(bissulfonyl)diazomethanes include 1,3-bis(phenylsulfonyldiazomethylsulfonyl)propane (compound A, decomposition point 135°C), 1,4-bis(phenylsulfonyldiazomethylsulfonyl)butane (compound B, decomposition point 147°C), 1,6-bis(phenylsulfonyldiazomethylsulfonyl)hexane (compound C, melting point 132°C, decomposition point 145°C), 1,10-
- 10 bis(phenylsulfonyldiazomethylsulfonyl)decane (compound D, decomposition point 147°C), 1,2-bis(cyclohexylsulfonyldiazomethylsulfonyl)ethane (compound E, decomposition point 149°C), 1,3-bis(cyclohexylsulfonyldiazomethylsulfonyl)propane (compound F, decomposition point 153°C), 1,6-
- 15 bis(cyclohexylsulfonyldiazomethylsulfonyl)hexane (compound G, melting point 109°C, decomposition point 122°C), 1,10-bis(cyclohexylsulfonyldiazomethylsulfonyl)decane (compound H, decomposition point 116°C).

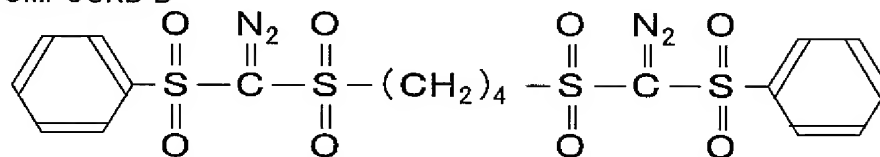
[0140]

[Chem 34]

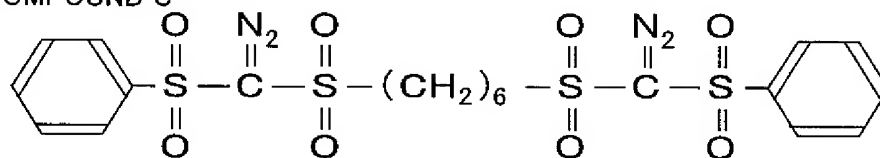
COMPOUND A



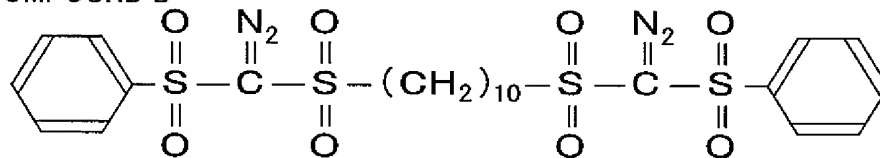
COMPOUND B



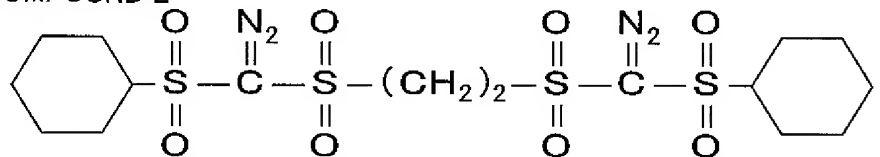
COMPOUND C



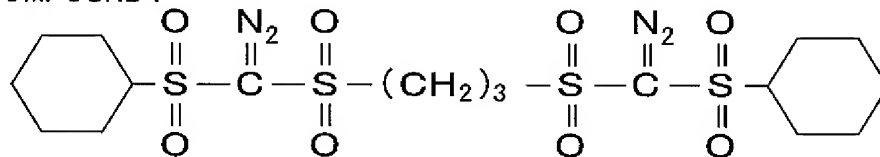
COMPOUND D



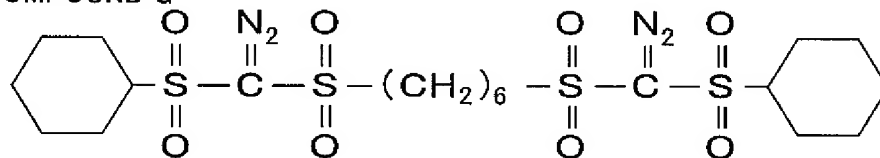
COMPOUND E



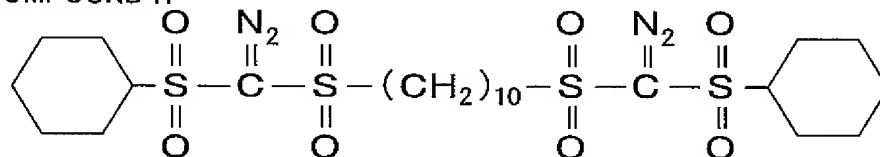
COMPOUND F



COMPOUND G



COMPOUND H



[0141]

An acid generator (B) can be used alone or in combination of two or more.

The content of an acid generator (B) is 0.5 to 30 parts by mass per 100 parts by mass of the component (A), preferably 1 to 15 parts by mass. When the content of an acid generator (B) is less than 0.5 parts by mass, the pattern formation may be not sufficiently. When the content of an acid generator (B) is out of the above range, a homogeneous solution is not obtained, and the storage stability may be poor.

[0142]

[Component (D)]

The photoresist composition can further include a nitrogen-containing organic compound (D) according to need. It is generally known that a small amount of a nitrogen-containing organic compound can be added to a chemically amplified resist composition as an acid diffusion inhibitor. In the present invention, a generally known nitrogen-containing organic compound can be added to the photoresist composition. Examples of the nitrogen-containing organic compound include an amine and an ammonium salt.

[0143]

Examples of the amine include an aliphatic secondary amine such as diethylamine, dipropylamine, dibutylamine, or dipentylamine; an aliphatic tertiary amine (a trialkylamine in which three alkyl groups bonded to nitrogen can be the same or different.) such as trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, N,N-dimethylpropylamine, N-ethyl-N-methylbutylamine, trihexylamine, triheptylamine, trioctylamine, tridecylamine, tridodecylamine, or tritetradecylamine; a tertiary alkanolamine such as N,N-dimethylmonoethanolamine, triisopropanolamine, N,N-diethylmonoethanolamine, triethanolamine, or tributanolamine; an aromatic tertiary amine such as N,N-dimethylaniline, N,N-diethylaniline, N-ethyl-N-methylaniline, N,N-dimethyltoluidine, N-methyldiphenylamine, N-ethyldiphenylamine, or triphenylamine.

[0144]

Examples of the ammonium salt include salts of a quaternary alkylammonium



ion such as an ammonium ion, a tetramethylammonium ion, a tetraethylammonium ion, a tetrapropylammonium ion, a tetrabutylammonium ion, or a tetrapentylammonium ion; and a hydroxyl group-containing organic carboxylic acid such as lactic acid.

Among them, preferable examples include a lower tertiary alkanolamine such as triethanolamine, triisopropanolamine, or tributanolamine; and a trialkylamine containing 6 to 15 carbon atoms such as trihexylamine, triheptylamine, trioctylamine, tridecanylamine, tridodecylamine, or tritetradecanylamine because these are excellent in reducing thickness loss in the top part of a fine resist pattern.

[0145]

A nitrogen-containing organic compound (D) can be used in a range of usually 0.01 to 5 parts by mass per 100 parts by mass of the base material component (A). When the content of a component (D) is less than 0.01 parts by mass, it is not possible to obtain an improvement in a pattern shape. When the content of a component (D) is more than 5 parts by mass, the diffusion of an acid is excessively inhibited, and the so-called exposure sensitivity is deteriorated.

[0146]

[Acid component]

Also, a photoresist composition of the present invention can further include an organic carboxylic acid, or an oxoacid of phosphorous or a derivative thereof as an optional component for the purpose of preventing the deterioration of sensitivity due to the addition of the nitrogen-containing organic compound (D).

[0147]

Preferable examples of the organic carboxylic acid include malonic acid, citric acid, malic acid, succinic acid, benzoic acid, and salicylic acid.

[0148]

Examples of the oxoacid of phosphorous or the derivative thereof include phosphoric acid or an ester derivative thereof such as phosphoric acid, di-n-butyl phosphate, or diphenyl phosphate; phosphonic acid or an ester derivative thereof such as phosphonic acid, dimethyl phosphonate, di-n-butyl phosphonate, phenylphosphonic acid,

diphenyl phosphonate, or dibenzyl phosphonate; and phosphinic acid or an ester derivative thereof such as phosphinic acid or phenylphosphinic acid, although phosphonic acid is particularly preferable among them. The organic carboxylic acid, or the oxoacid of phosphorous or the derivative thereof can be used in a range of 0.01 to 5.0 parts by mass per 100 parts by mass of the base material component (A).

[0149]

[Organic solvent (E)]

The photoresist composition of the present invention can be produced by dissolving the base material resin component (A), the acid generator (B), the nitrogen-containing organic compound (D), and optional components according to need in an organic solvent (E) to be a homogeneous solution. One, or two or more organic solvents (E) can be selected to be used from among known solvents for a chemically amplified resist.

[0150]

Examples of the organic solvent include ketones such as  $\gamma$ -butyrolactone, acetone, methyl ethyl ketone, cyclohexanone, methyl isoamyl ketone, or 2-heptanone; polyhydric alcohols and derivatives thereof such as ethylene glycol, ethylene glycol monoacetate, diethylene glycol, diethylene glycol monoacetate, propylene glycol, propylene glycol monoacetate, dipropylene glycol, or the monomethyl ether, monoethyl ether, monopropyl ether, monobutyl ether, or monophenyl ether of dipropylene glycol monoacetate; cyclic ethers such as dioxane; and esters such as methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate, or ethyl ethoxypropionate. These organic solvents can be used alone, or in a mixed solvent of two or more different solvents. The mixed solvent of propylene glycol monomethyl ether acetate (PGMEA) and a polar solvent is preferable, and the mixture ratio can be appropriately determined in consideration of miscibility of PGMEA and a polar solvent although the mass ratio of PGMEA:(polar solvent) is preferably within a range of 1:9 to 8:2, more preferably 2:8 to 5:5, most preferably 3:7 to 4:6..

[0151]

Specifically, in the case of blending ethyl lactate (EL) as a polar solvent, the mass ratio of PGMEA:EL is preferably 2:8 to 5:5, more preferably 3:7 to 4:6. Also, the mixed solvent of  $\gamma$ -butyrolactone and at least one selected from PGMEA and EL is  
5 preferable as an organic solvent. In this case, as for the mixture ratio, the mass ratio of the former and the latter is preferably 70:30 to 95:5. The amount of a component (E) is not specifically limited and is appropriately determined according to the thickness of a coating film and the concentration capable of coating on a substrate. Generally, the concentration of a solid part of a photoresist composition is 2 to 20 mass%, preferably 5  
10 to 15 mass%.

[0152]

[Other components]

Also, a photoresist composition of the present invention can further include miscible additives such as generally known dissolution inhibitors, additive resins for  
15 improving properties of a photoresist film, surfactants for improving coating property, plasticizers, stabilizers, colorants, and halation prevention agents according to need.

[0153]

Also, a compound containing an alcoholic hydroxyl group, a phenolic hydroxyl group, or a carboxyl group, each being protected by an acid dissociable, dissolution  
20 inhibiting group (ii) of the present invention, can be used as a dissolution inhibitor. Preferable examples of the dissolution inhibitor include a compound in which an acid dissociable, dissolution inhibiting group (ii) of the present invention protects an alkali soluble group (i), particularly an alcoholic hydroxyl group, a phenolic hydroxyl group, or a carboxyl group, in monomer components corresponding to the structural units  
25 represented by the chemical formulae (21) to (35). In a photoresist composition including the aforementioned compound as an acid dissociable, dissolution inhibitor (C) with the base material resin (A), a dissolution inhibiting effect in an alkali development is shown before exposure, whereas alkali solubility due to deprotection is shown after exposure. Therefore, it is possible to prevent thickness loss of a resist pattern and to

provide a fine pattern with high resolution.

[0154]

In particular, a compound of the present invention contains an acid dissociable, dissolution inhibiting group containing a cycloaliphatic group in this molecule; therefore, the alkali solubility is greatly changed under the action of an acid. Accordingly, according to a polymer compound of the present invention including the structural unit derived from the compound, it is possible to obtain a photoresist composition in which rectangularity, resolution, and sensitivity are favorable in the system of a chemically amplified positive resist, and favorable photoresist characteristics are expressed because an acid dissociable, dissolution inhibiting group can be dissociated by an acid generator generating a weak acid.

[0155]

Moreover, in a photoresist composition of the present invention, etching resistance can be improved. In particular, when a hydrophilic group is introduced into a photoresist composition of the present invention, the adhesion of a resist pattern to a substrate is improved, and the effect of reducing developing defects can be obtained due to the improvement of the affinity of a resist pattern to an alkali developing solution.

A photoresist composition of the present invention is preferably used for patterning of a semiconductor integrated circuit by means of lithography. In particular, an excellent resolution property can be obtained in fine patterning by using a light source with a wavelength of 300 nm or less, for example a KrF, ArF, or F<sub>2</sub> excimer laser. Among them, an ArF excimer laser is most preferable. Moreover, a photoresist composition of the present invention is applicable to an electron beam.

[0156]

A resist pattern formation method of the present invention includes forming a photoresist film on a substrate using the aforementioned photoresist composition; exposing the photoresist film; and developing the photoresist film to form a resist pattern.

[0157]

A photoresist composition of the present invention forms a resist pattern

according to a conventional lithography process. This process is as follows. Firstly, a photoresist composition is coated on a substrate by means of spin-coating or the like, and then dried to form a photoresist film. Next, the photoresist film is selectively exposed through a mask pattern, and then Post Exposure Baking (PEB) is performed. Finally, the exposed photoresist film is developed using an alkaline aqueous solution to form a resist pattern. Herein, a post baking process can be performed according to need.

There is no limitation regarding the light source, although examples of the light source include a far-UV ray with a wavelength of 200 nm or less, specifically an ArF excimer laser, an F<sub>2</sub> excimer laser, EUV (extreme ultraviolet light), an electron beam, soft X ray, and X ray. Particularly preferable examples of the light source include a KrF excimer laser, an ArF excimer laser, and an F<sub>2</sub> excimer laser. In the case of using a polymer compound (copolymer) using a novel compound of the present invention, an ArF excimer laser is particularly preferable.

[0158]

The conditions for a resist pattern formation method including the rotation number of the resist coating, the prebaking temperature, exposure conditions, Post Exposure Baking (PEB) conditions, alkali development conditions can be those conventionally used. In detail, the rotation number is about 1,200 to 3,500 rpm, specifically about 2,000 rpm. The prebaking (PB) temperature is within a range of 70°C to 130°C. These conditions form a resist film with a thickness of 80 to 300 nm. Exposure can be performed through a mask. A conventional binary mask or a phase-shift mask can be used as a mask for selective exposure. The temperature of Post Exposure Baking (PEB) is within a range of 90°C to 140°C. As for alkali development conditions, the development is performed using a 1% to 5% by mass of TMAH (tetramethyl ammonium hydroxide) developer at a temperature of 23°C, for 15 to 90 seconds, followed by rinsing with water.

[Examples]

[0159]

(Synthesis example 1) Synthesis of 4-oxo-2-adamantyl chloromethyl ether

(The compound represented by the following chemical formula (58). Hereinafter, the compounds in Examples may be referred to as a compound name followed by a formula number such as (58).)

Paraformaldehyde was added to 4-oxo-2-hydroxyadamantane, and a hydrogen chloride gas was injected at 2.5 equivalent amounts per this 4-oxo-2-hydroxyadamantane. Then, the reaction was conducted at a temperature of 50°C for 12 hours. After the completion of the reaction, the product was distilled under reduced pressure so as to obtain 4-oxo-2-adamantyl chloromethyl ether (compound 1) represented by the following chemical formula (58).

10 [0160]

(Synthesis example 2) Synthesis of 2-adamantyl chloromethyl ether (59)

Paraformaldehyde was added to 2-hydroxyadamantane, and a hydrogen chloride gas was injected at 2.5 equivalent amounts per this 2-hydroxyadamantane. Then, the reaction was conducted at a temperature of 50°C for 12 hours. After the completion of the reaction, the product was distilled under reduced pressure so as to obtain 2-adamantyl chloromethyl ether (compound 2) represented by the following chemical formula (59).

[0161]

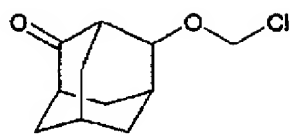
(Synthesis example 3) Synthesis of 1-adamantylmethyl chloromethyl ether (60)

20 Paraformaldehyde was added to adamantane-1-methanol, and a hydrogen chloride gas was injected at 2.5 equivalent amounts per this adamantane-1-methanol. Then, the reaction was conducted at a temperature of 50°C for 12 hours. After the completion of the reaction, the product was distilled under reduced pressure so as to obtain 1-adamantylmethyl chloromethyl ether (compound 3) represented by the following chemical formula (60).

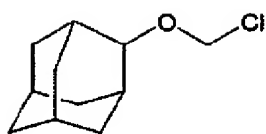
[0162]

[Chem 35]

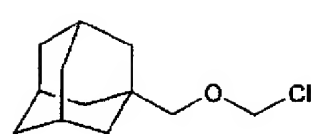
59



(58)



(59)



(60)

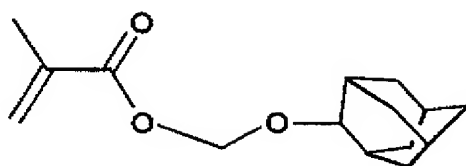
[0163]

(Synthesis example 4) Synthesis of 2-adamantyloxymethyl methacrylate (61)

In 200 mL of tetrahydrofuran, 6.9 g of methacrylic acid was dissolved, and then  
 5 8.0 g of triethylamine was added. After stirring at room temperature, 100 mL of  
 tetrahydrofuran, in which 15 g of the compound 2 (59) was dissolved, was added  
 dropwise. After stirring at room temperature for 12 hours, the precipitated salt was  
 removed by filtration. The obtained filtrate was evaporated, dissolved in 200 mL of  
 ethyl acetate, washed with pure water (100 mL×3), and then evaporated again. After  
 10 leaving at freezing point or lower, a white solid substance was obtained. This compound  
 is referred to as the compound 4 and represented by the chemical formula (61). The  
 infrared absorption spectra (IR) and the proton nuclear magnetic resonance spectra (<sup>1</sup>H-  
 NMR) of the compound 4 were measured, and the results are as follows: IR (cm<sup>-1</sup>): 2907,  
 2854 (C-H stretch), 1725 (C=O vibration), 1638 (C=C stretch); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, internal  
 15 standard: tetramethylsilane) ppm: 1.45-2.1 (m, 17H), 3.75 (s, 1H), 5.45 (s, 2H), 5.6 (s,  
 1H), 6.12 (s, 1H)

[0164]

[Chem 36]



(61)

20

[0165]

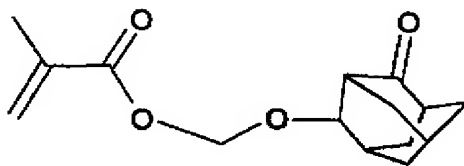
(Synthesis example 5) Synthesis of 4-oxo-2-adamantyloxymethyl

methacrylate (62)

In 50 mL of tetrahydrofuran, 2.2 g of methacrylic acid was dissolved, and then 2.5 g of triethylamine was added. After stirring at room temperature, 50 mL of tetrahydrofuran, in which 4.3 g of the compound 1 (58) was dissolved, was added dropwise. After stirring at room temperature for 12 hours, the precipitated salt was removed by filtration. The obtained filtrate was evaporated, dissolved in 100 mL of ethyl acetate, washed with pure water (50 mL×3), and then evaporated again. After leaving at freezing point or lower, a white solid substance was obtained. This compound is referred to as the compound 5 and represented by chemical formula (62). The infrared absorption spectra (IR) and the proton nuclear magnetic resonance spectra ( $^1\text{H-NMR}$ ) of the compound 5 were measured, and the results are as follows: IR ( $\text{cm}^{-1}$ ): 2926, 2861 (C-H stretch), 1725 (C=O stretch), 1636 (C=C stretch);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , internal standard: tetramethylsilane) ppm: 1.62-3.85 (m, 15H), 4.2 (s, 1H), 5.4 (s, 2H), 5.65 (s, 1H), 6.15 (s, 1H)

[0166]

[Chem 37]



(62)

[0167]

(Synthesis example 6) Synthesis of 1-adamantylmethyloxymethyl methacrylate (63)

In 200 mL of tetrahydrofuran, 5.5 g of methacrylic acid was dissolved, and then 6.5 g of triethylamine was added. After stirring at room temperature, 100 mL of tetrahydrofuran, in which 12.9 g of the compound 3 (60) was dissolved, was added dropwise. After stirring at room temperature for 12 hours, the precipitated salt was

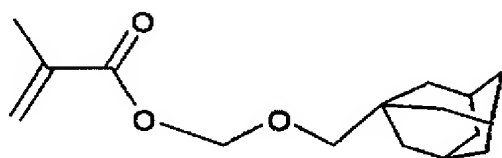


removed by filtration. The obtained filtrate was evaporated, dissolved in 100 mL of ethyl acetate, washed with pure water (100 mL×3), and then evaporated again so as to obtain a colorless oily compound. This compound is referred to as the compound 6 and represented by chemical formula (63). The infrared absorption spectra and the proton nuclear magnetic resonance spectra ( $^1\text{H-NMR}$ ) of the compound 6 were measured, and the results are as follows: IR ( $\text{cm}^{-1}$ ): 2904, 2850 (C-H stretch), 1727 (C=O stretch), 1638 (C=C vibration);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , internal standard: tetramethylsilane) ppm: 1.46-1.96 (m, 18H), 3.22 (s, 2H), 5.34 (s, 2H), 5.6 (s, 1H), 6.15 (s, 1H)

[0168]

10

[Chem 37]



(63)

[0169]

&lt;Synthesis of resins 1 to 5 containing the structural unit (a1)&gt;

15

(Synthesis example 7) Synthesis of resin 1 (The polymer compound represented by the following chemical formula (64). Hereinafter, the polymer compounds in Examples may be referred to as a resin number followed by a formula number such as (64).)

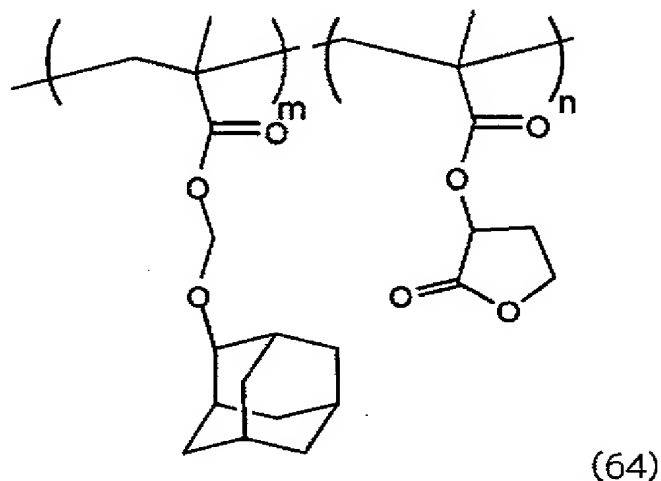
In 50 mL of tetrahydrofuran, 8.0 g of the compound 4 and 5.4 g of  $\gamma$ -butyrolactone methacrylate were dissolved, and then 0.52 g of azobisisobutyronitrile was added. After refluxing for 24 hours, the reaction solution was added dropwise to 1 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. This resin is referred to as the resin 1 and represented by the chemical formula (64). The molecular weight ( $M_w$ ) of the resin 1 was 21,100. Also, the carbon 13 (hereinafter, carbon 13 means carbon with a

mass number of 13.) nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results showed that the composition ratio (hereinafter, the unit of composition ratio is mol%.) in the chemical formula was  $m:n = 0.49:0.51$ .

[0170]

5

[Chem 39]



[0171]

(Synthesis example 8) Synthesis of resin 2 (65)

10

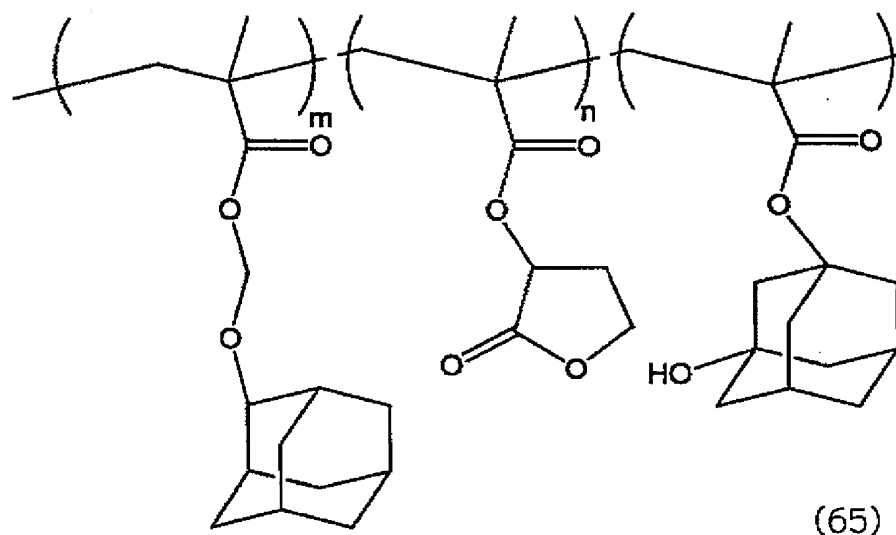
In 20 mL of tetrahydrofuran, 1.0 g of the compound 4, 0.68 g of  $\gamma$ -butyrolactone methacrylate, and 0.47 g of 3-hydroxy-1-adamantyl methacrylate were dissolved, and then 0.08 g of azobisisobutyronitrile was added. After refluxing for 24 hours, the reaction solution was added dropwise to 2 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. This resin is referred to as the resin 2 and represented by the chemical formula (65). The molecular weight ( $M_w$ ) of the resin 2 was 11,500. Also, the carbon  $^{13}$  nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results showed that the composition ratio in the chemical formula was  $m:n:l = 0.34:0.42:0.24$ .

15

[0172]

20

[Chem 40]



[0173]

(Synthesis example 9) Synthesis of resin 3 (66)

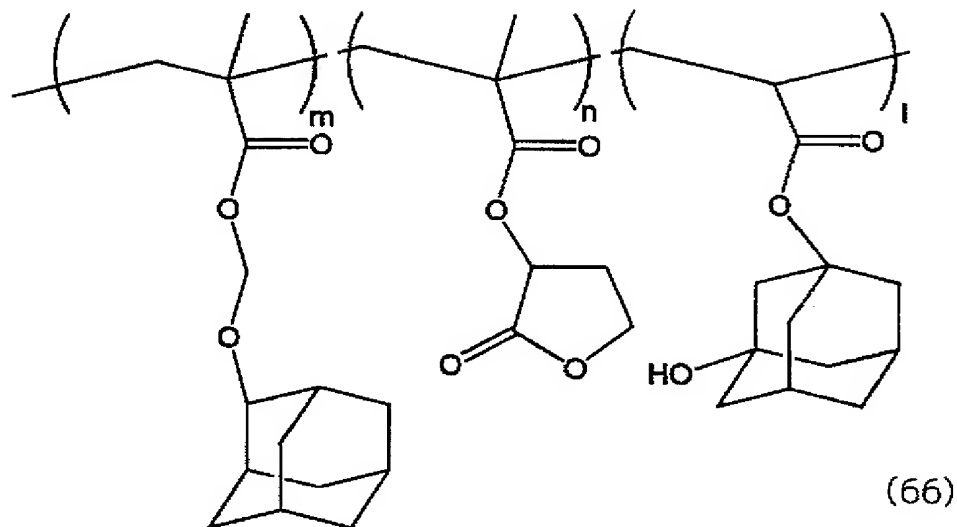
5 In 20 mL of tetrahydrofuran, 1.0 g of the compound 4, 0.68 g of  $\gamma$ -butyrolactone methacrylate, and 0.44 g of 3-hydroxy-1-adamantyl acrylate were dissolved, and then 0.08 g of azobisisobutyronitrile was added. After refluxing for 24 hours, the reaction solution was added dropwise to 2 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was

10 obtained. This resin is referred to as the resin 3 and represented by the chemical formula (66). The molecular weight (Mw) of the resin 3 was 10,800. Also, the carbon 13 nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results showed that the composition ratio was  $m:n:l = 0.29:0.45:0.26$ .

[0174]

15

[Chem 41]



[0175]

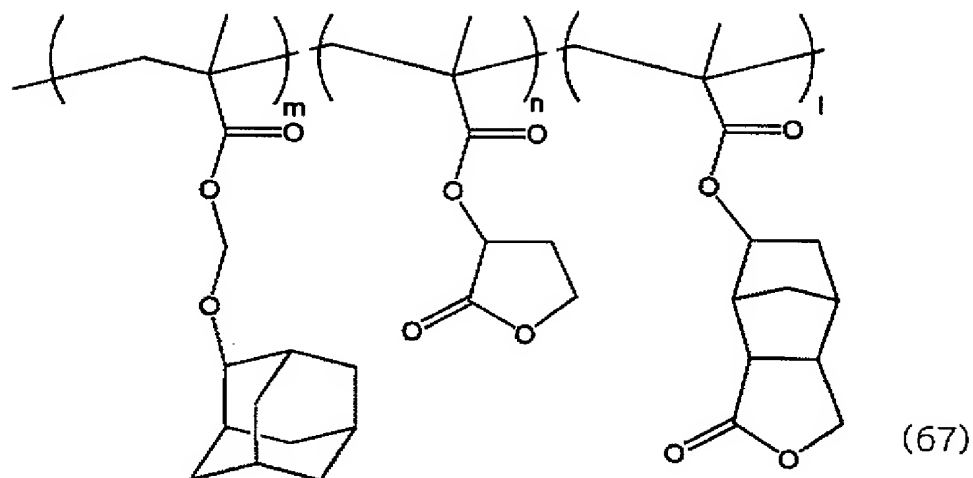
(Synthesis example 10) Synthesis of resin 4 (67)

In 20 mL of tetrahydrofuran, 1.0 g of the compound 4, 0.68 g of  $\gamma$ -butyrolactone methacrylate, and 0.44 g of norbornane-lactone methacrylate (a monomer corresponding to a structural unit represented by the general formula (49) in which  $R^3$  represents a methyl group) were dissolved, and then 0.08 g of azobisisobutyronitrile was added. After refluxing for 24 hours, the reaction solution was added dropwise to 2 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. This resin is referred to as the resin 4 and represented by the chemical formula (67). The molecular weight ( $M_w$ ) of the resin 4 was 12,000. Also, the carbon 13 nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results showed that the composition ratio was  $m:n:l = 0.37:0.42:0.21$ .

[0176]

15

[Chem 42]



[0177]

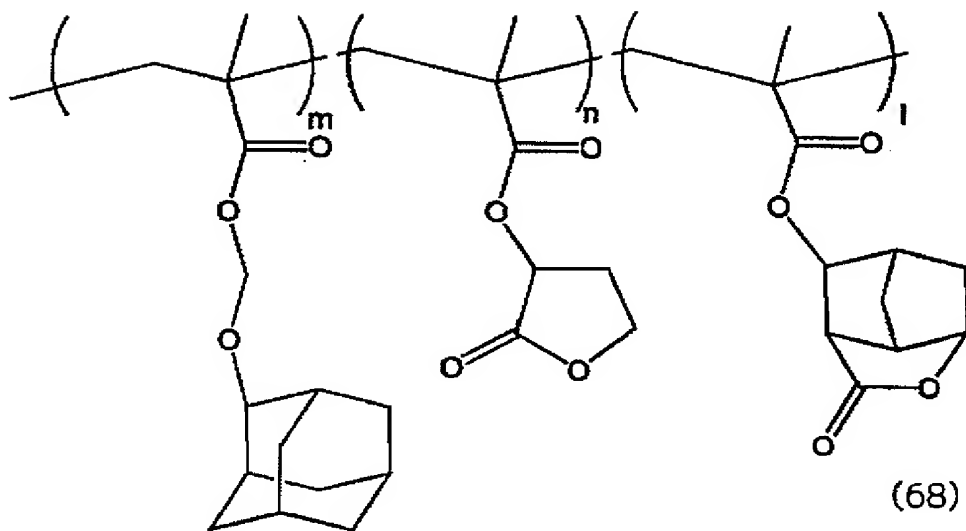
(Synthesis example 11) Synthesis of resin 5 (68)

In 20 mL of tetrahydrofuran, 1.0 g of the compound 4, 0.68 g of  $\gamma$ -butyrolactone methacrylate, and 0.44 g of norbornane-lactone methacrylate (a monomer corresponding to a structural unit represented by the general formula (48) in which  $R^3$  represents a methyl group) were dissolved, and then 0.08 g of azobisisobutyronitrile was added. After refluxing for 24 hours, the reaction solution was added dropwise to 2 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. This resin is referred to as the resin 5 and represented by the chemical formula (68). The molecular weight ( $M_w$ ) of the resin 5 was 12,900. Also, the carbon 13 nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results showed that the composition ratio was  $m:n:l = 0.36:0.42:0.22$ .

[0178]

15

[Chem 43]



[0179]

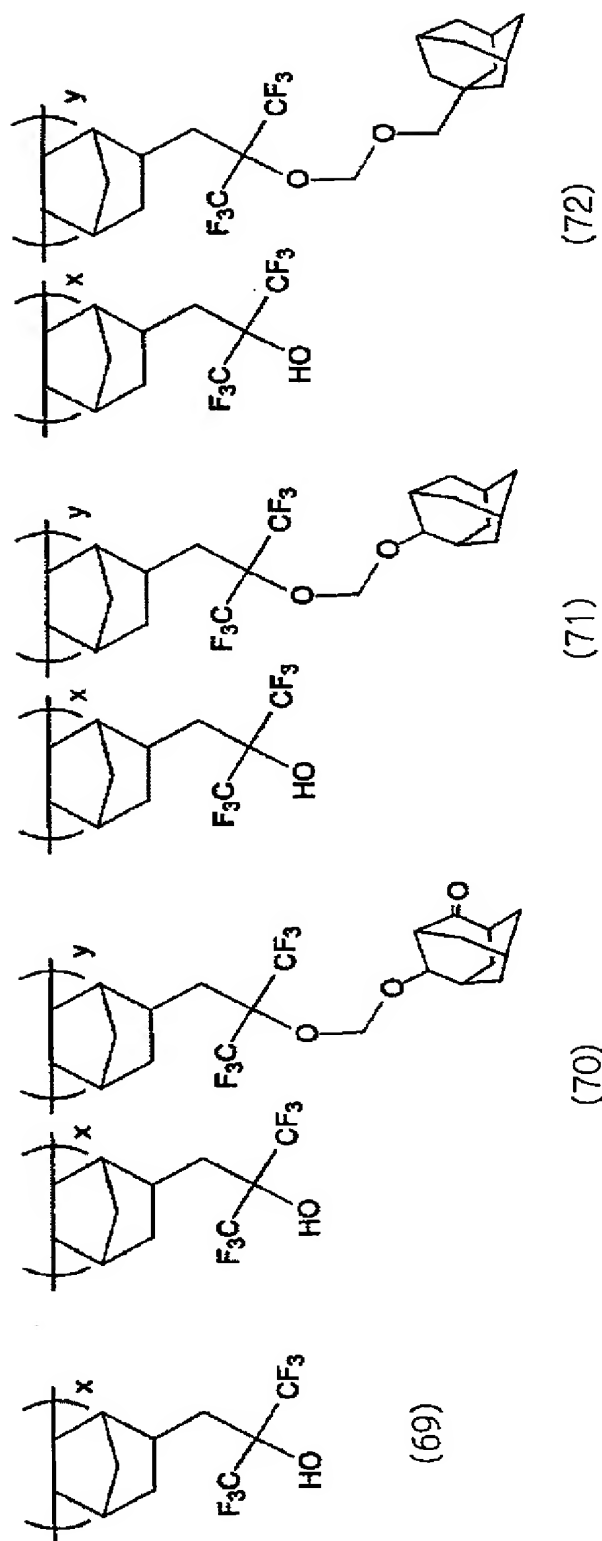
<Synthesis of resins 7 to 9 in which an alkali soluble group is an alcoholic hydroxyl group>

5        The following resin 6 synthesized by addition polymerization was used to obtain the resins 7 to 9 in which the compounds 1 to 3 were introduced, respectively. The resins 6 to 9 are represented by the following chemical formulae (69) to (72). The physical properties values of these resins are shown in Table 1.

[0180]

10

[Chem 44]



(Synthesis of resin 6 (69))

The resin 6 represented by the chemical formula (69) was synthesized by addition polymerization using a known metal catalyst. In the chemical formula, x represents 100.

5 [0182]

(Synthesis example 12) Synthesis of resin 7 (70)

In 70 mL of tetrahydrofuran, 5.0 g of the resin 6 was dissolved, and then 0.15 g of sodium hydride was added. After stirring until the solution system became homogeneous at room temperature, 0.8 g of the compound 1 was added dropwise. After  
10 stirring at room temperature for 12 hours, the precipitated salt was removed by filtration. The obtained filtrate was added dropwise to 1 L of water. The precipitated resin was separated by filtration, dried under reduced pressure, and then dissolved in tetrahydrofuran. This resin solution was added dropwise to 1 L of a mixed solvent of methanol: pure water (80:20). The precipitated resin was separated by filtration and  
15 dried under reduced pressure, and then a white powder resin was obtained. This resin is referred to as the resin 7.

[0183]

(Synthesis example 13) Synthesis of resin 8 (71)

In 70 mL of tetrahydrofuran, 5.0 g of the resin 6 was dissolved, and then 0.15 g  
20 of sodium hydride was added. After stirring until the solution system became homogeneous at room temperature, 0.7 g of the compound 2 was added dropwise. After stirring at room temperature for 12 hours, the precipitated salt was removed by filtration. The obtained filtrate was added dropwise to 1 L of water. The precipitated resin was separated by filtration, dried under reduced pressure, and then dissolved in  
25 tetrahydrofuran. This resin solution was added dropwise to 1 L of a mixed solvent of methanol: pure water (80:20). The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. This resin is referred to as the resin 8.

[0184]



## (Synthesis example 14) Synthesis of resin 9 (72)

In 70 mL of tetrahydrofuran, 5.0 g of the resin 6 was dissolved, and then 0.15 g of sodium hydride was added. After stirring until the solution system became homogeneous at room temperature, 0.8 g of the compound 3 was added dropwise. After stirring at room temperature for 12 hours, the precipitated salt was removed by filtration. The obtained filtrate was added dropwise to 1 L of water. The precipitated resin was separated by filtration, dried under reduced pressure, and then dissolved in tetrahydrofuran. This resin solution was added dropwise to 1 L of a mixed solvent of methanol: pure water (80:20). The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. This resin is referred to as the resin 9.

[0185]

(Table 1)

Physical properties values of resins 6 to 9

	Molecular weight (Mw)	Degree of dispersion (Mw / Mn)	Composition ratio (x / y)
Resin 6	8,500	—	—
Resin 7	10,900	1.49	0.78 / 0.22
Resin 8	13,400	1.37	0.81 / 0.19
Resin 9	10,800	1.37	0.73 / 0.27

[0186]

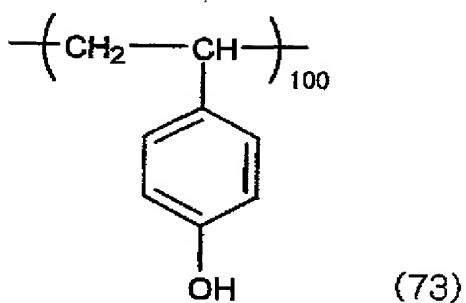
<Synthesis of the resin 10 (74) in which an alkali soluble group is a phenolic hydroxyl group>

5           (Synthesis example 15) Synthesis of resin 10 (74)

In 200 mL of tetrahydrofuran, 24.0 g of a poly-4-hydroxystyrene resin (73) represented by the following chemical formula (73) was dissolved, and then 2.4 g of sodium hydride was added. After stirring until the solution system became homogeneous at room temperature, 12 g of the compound 2 was added dropwise. After stirring at room temperature for 12 hours, the precipitated salt was removed by filtration. The obtained filtrate was added dropwise to 1 L of water. The precipitated resin was separated by filtration, dried under reduced pressure, and then dissolved in tetrahydrofuran. This resin solution was added dropwise to 3 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin 10 was obtained. The molecular weight (Mw) and the degree of dispersion (Mw / Mn) of the resin 10 were 12,400 and 1.28, respectively. Also, the proton nuclear magnetic resonance spectra (<sup>1</sup>H-NMR) were measured, and the results showed that the composition ratio in the chemical formula (74) was m: n = 0.87:0.13.

[0187]

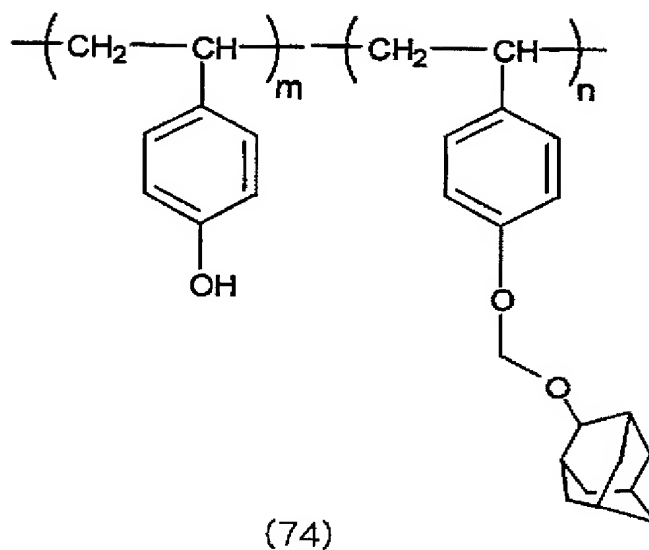
20           [Chem 45]



[0188]

[Chem 46]

5



[0189]

&lt;Synthesis of the resins 11 to 14 containing the structural unit (a1)&gt;

(Synthesis example 16) Synthesis of resin 11 (75)

10

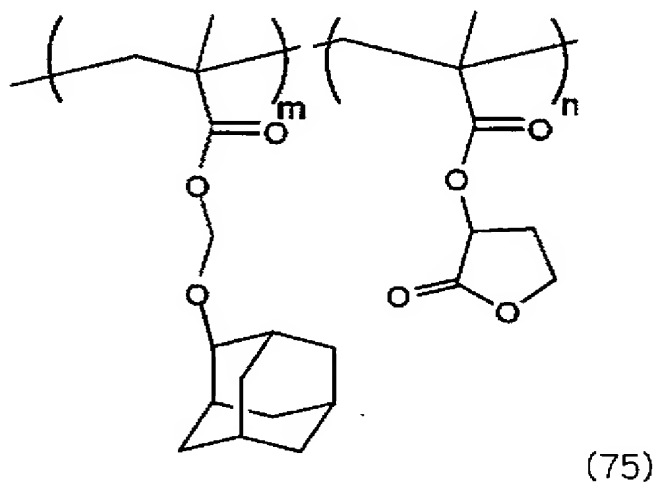
In 45 mL of tetrahydrofuran, 3.0 g of the compound 4 and 2.0 g of  $\gamma$ -butyrolactone methacrylate were dissolved, and then 0.20 g of azobisisobutyronitrile was added. After refluxing for 12 hours, the reaction solution was added dropwise to 2 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced

pressure, and then a white powder resin was obtained. This resin is referred to as the resin 11 and represented by the chemical formula (75). The molecular weight ( $M_w$ ) and the degree of dispersion ( $M_w / M_n$ ) of the resin 11 were 12,300 and 1.96, respectively. Also, the carbon 13 nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results showed that the composition ratio in the chemical formula was  $m:n = 0.47:0.53$ . Also, the heat decomposition point and the  $T_g$  were  $257.1^\circ\text{C}$  and  $147.9^\circ\text{C}$ , respectively.

In the present synthesis examples and the comparative synthesis examples, a heat decomposition point was measured by using a thermal analysis apparatus, DSC6200 (manufactured by Seiko Instruments Inc.), under the condition of an increasing temperature of  $10^\circ\text{C}/\text{min}$ , and  $T_g$  (glass transition temperature) was measured by using a thermal analysis apparatus, TG/DTA6200 (manufactured by Seiko Instruments Inc.), under the condition of an increasing temperature of  $10^\circ\text{C}/\text{min}$ .

[0190]

[Chem 47]



[0191]

(Synthesis example 17) Synthesis of resin 12 (77)

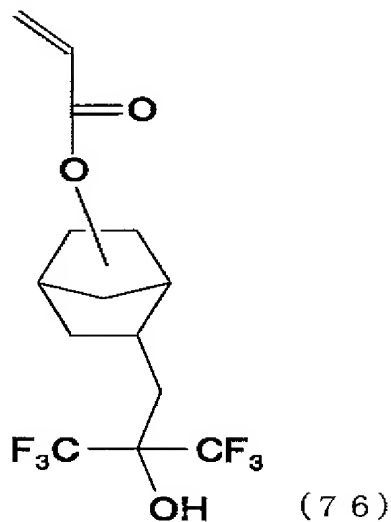
In 60 mL of tetrahydrofuran, 3.0 g of the compound 4 and 4.0 g of the compound 7 represented by the following chemical formula (76) were dissolved, and then 0.20 g of azobisisobutyronitrile was added. After refluxing for 12 hours, the reaction solution was

added dropwise to 2 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. This resin is referred to as the resin 12 and represented by the chemical formula (77). The molecular weight ( $M_w$ ) and the degree of dispersion ( $M_w / M_n$ ) of the resin 12 were 9,800 and 1.61, respectively. Also, the carbon 13 nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results showed that the composition ratio in the chemical formula was  $m:n = 0.57:0.43$ . Also, the heat decomposition point and the  $T_g$  were  $234.5^\circ\text{C}$  and  $114.1^\circ\text{C}$ , respectively.

[0192]

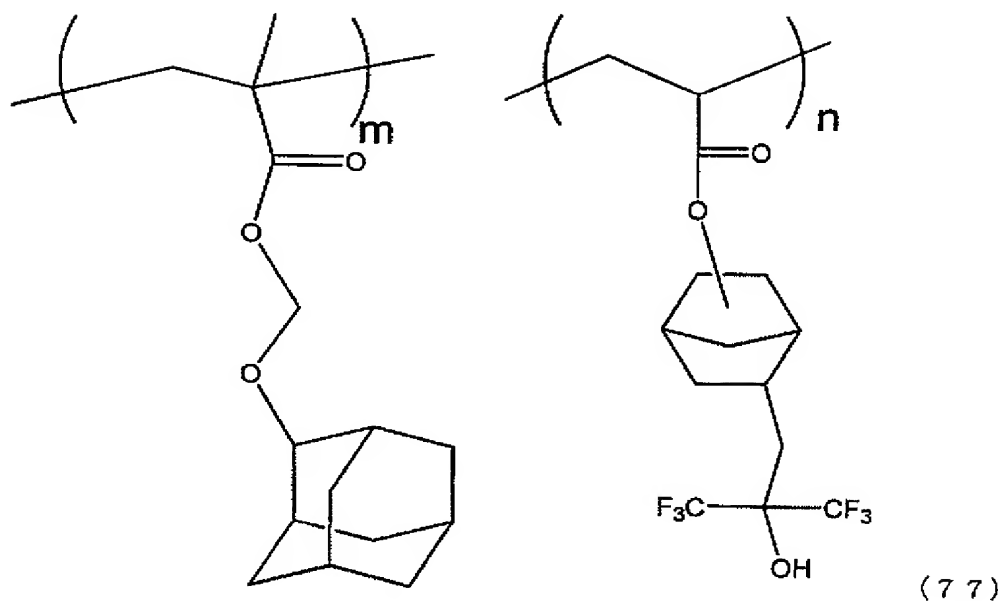
10

[Chem 48]



[0193]

[Chem 49]



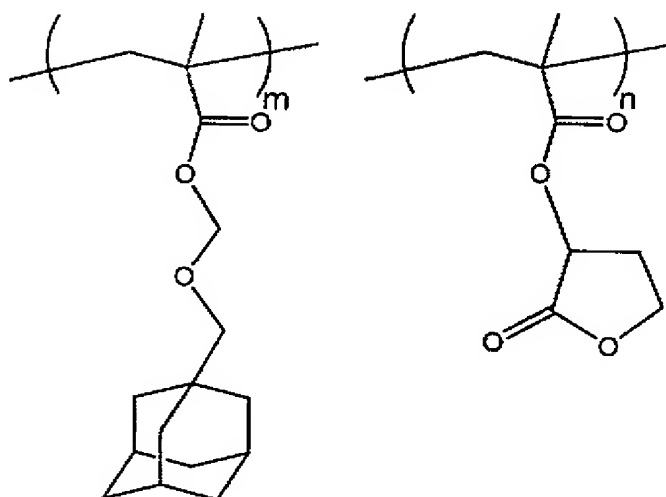
[0194]

(Synthesis example 18) Synthesis of resin 13 (78)

In 90 mL of tetrahydrofuran, 6.0 g of the compound 6 and 3.9 g of  $\gamma$ -butyrolactone methacrylate were dissolved, and then 0.37 g of azobisisobutyronitrile was added. After refluxing for 12 hours, the reaction solution was added dropwise to 2 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. This resin is referred to as the resin 13 and represented by the chemical formula (78). The molecular weight (Mw) and the degree of dispersion (Mw / Mn) of the resin 13 were 12,800 and 1.87, respectively. Also, the carbon 13 nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results showed that the composition ratio in the chemical formula was m: n = 0.43:0.57. Also, the heat decomposition point and the Tg were 240.0°C and 142.2°C, respectively.

[0195]

[Chem 50]



( 7 8 )

[0196]

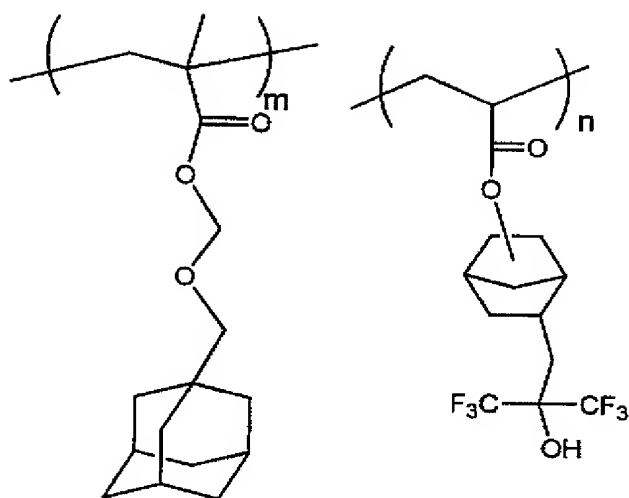
(Synthesis example 19) Synthesis of resin 14 (79)

In 120 mL of tetrahydrofuran, 6.0 g of the compound 6 and 7.6 g of the  
 5 compound 7 were dissolved, and then 0.37 g of azobisisobutyronitrile was added. After  
 refluxing for 12 hours, the reaction solution was added dropwise to 2 L of n-heptane.  
 The precipitated resin was separated by filtration and dried under reduced pressure, and  
 then a white powder resin was obtained. This resin is referred to as the resin 14 and  
 represented by the chemical formula (79). The molecular weight ( $M_w$ ) and the degree  
 10 of dispersion ( $M_w / M_n$ ) of the resin 14 were 11,600 and 1.60, respectively. Also, the  
 carbon 13 nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results  
 showed that the composition ratio in the chemical formula was  $m:n = 0.56:0.44$ . Also,  
 the heat decomposition point and the  $T_g$  were 233.6°C and 109.4°C, respectively.

[0197]

15

[Chem 51]



( 7 9 )

[0198]

&lt;Synthesis of comparative resins 1 to 4 as Comparative examples&gt;

(Comparative synthesis example 1) Synthesis of comparative resin 1 (80)

5 In 140 mL of tetrahydrofuran, 9.9 g of 2-methyl-2-adamantyl methacrylate and 6.0 g of  $\gamma$ -butyrolactone methacrylate were dissolved, and then 0.63 g of azobisisobutyronitrile was added. After refluxing for 12 hours, the reaction solution was added dropwise to 2 L of n-heptane. The precipitated resin was separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. This

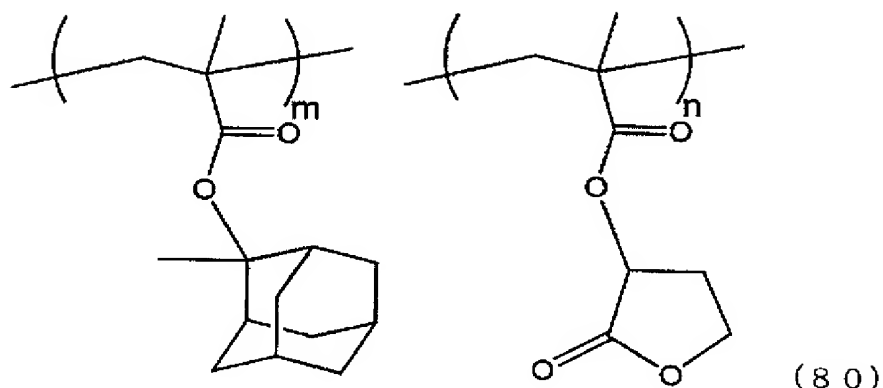
10 resin is referred to as the comparative resin 1 and represented by the chemical formula (80). The molecular weight (Mw) and the degree of dispersion (Mw / Mn) of the comparative resin 1 were 8,700 and 1.83, respectively. Also, the carbon 13 nuclear magnetic resonance spectra ( $^{13}\text{C}$ -NMR) were measured, and the results showed that the composition ratio in the chemical formula was m:n = 0.41:0.59. Also, the heat

15 decomposition point and the Tg were 222.5°C and 158.9°C, respectively.

[0199]

[Chem 52]





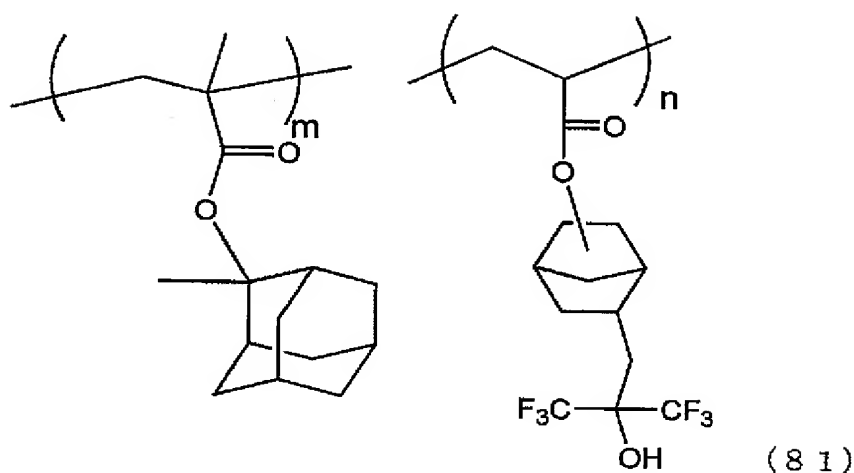
[0200]

(Comparative synthesis example 2) Synthesis of comparative resin 2 (81)

In 230 mL of tetrahydrofuran, 10.6 g of 2-methyl-2-adamantyl methacrylate and  
 5 15.0 g of the compound 7 were dissolved, and then 0.74 g of azobisisobutyronitrile was  
 added. After refluxing for 12 hours, the reaction solution was added dropwise to 2 L of  
 n-heptane. The precipitated resin was separated by filtration and dried under reduced  
 pressure, and then a white powder resin was obtained. This resin is referred to as the  
 comparative resin 2 and represented by the chemical formula (81). The molecular  
 10 weight (Mw) and the degree of dispersion (Mw / Mn) of the comparative resin 2 were  
 8,780 and 1.42, respectively. Also, the carbon 13 nuclear magnetic resonance spectra  
 (<sup>13</sup>C-NMR) were measured, and the results showed that the composition ratio in the  
 chemical formula was m:n = 0.64:0.36. Also, the heat decomposition point and the Tg  
 were 215.7°C and 133.3°C, respectively.

15 [0201]

[Chem 53]



[0202]

(Comparative synthesis example 3) Synthesis of comparative resin 3 (83)

5 In 100 mL of tetrahydrofuran, 15 g of the comparative resin 3' (manufactured by Promerus LLC; weight average molecular weight = 7,640, degree of dispersion = 1.93) represented by the following chemical formula (82) was dissolved, and then 0.88 g of sodium hydride was added. After stirring until the solution system became homogeneous at room temperature, 1.76 g of chloromethyl methyl ether (manufactured

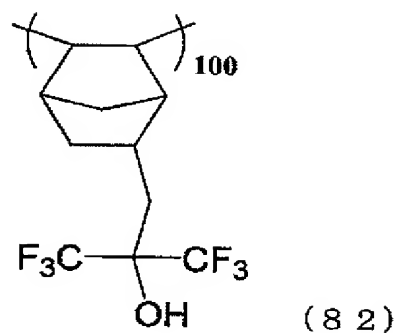
10 by Tokyo Ohka Kogyo Co., Ltd.) was added dropwise. After stirring at room temperature for 12 hours, the precipitated salt was removed by filtration. The obtained filtrate was added dropwise to 1 L of water. The precipitated resin was separated by filtration, dried under reduced pressure, and then dissolved in tetrahydrofuran. This resin solution was added dropwise to 1 L of n-heptane. The precipitated resin was

15 separated by filtration and dried under reduced pressure, and then a white powder resin was obtained. The yield was 5.0 g. This resin is referred to as the comparative resin 3 and represented by the chemical formula (83). The weight average molecular weight (Mw) and the degree of dispersion (Mw / Mn) of the comparative resin 3 were 14,000 and 2.14, respectively. The protection rate of a hydroxyl group was 40.7%.

20

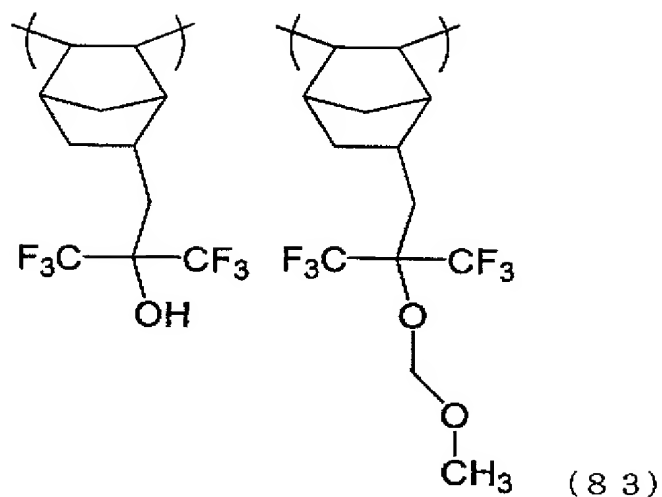
[0203]

[Chem 54]



[0204]

[Chem 55]



5

[0205]

(Comparative synthesis example 4) Synthesis of comparative resin 4 (83)

The protection rate was changed in Comparative synthesis example 3. In other words, the reaction was conducted by using the same process other than adjusting the amount of chloromethyl methyl ether. The weight average molecular weight (Mw) and the degree of dispersion (Mw / Mn) of the obtained resin were 13,900 and 2.23, respectively. The protection rate of a hydroxyl group was 20.8%. This resin is referred to as the comparative resin 4 and represented by the chemical formula (83).

[0206]

(Examples 1 to 3) Confirmation of the exposure resolution of a positive photoresist

The resolution of a positive photoresist was confirmed by using the resins 7 to 9.

- 5 An ArF excimer laser was used for exposure. The positive photoresist composition was prepared by mixing each of the resins 7 to 9 with the acid generator, the nitrogen-containing organic compound, and the solvent, each being described below.

	Resins 7 to 9	100 parts
	by mass	
10	Acid generator: TPS-PFBS	2.0 parts
	by mass	
	Nitrogen-containing organic compound: triisopropanolamine	0.2 parts
	by mass	
	Organic solvent: PGMEA	1250 parts
15	by mass	

[0207]

“TPS-PFBS” represents triphenylsulfonium perfluorobutanesulfonate, and “PGMEA” represents propylene glycol monomethyl ether acetate.

[0208]

- 20 The exposure resolution of the positive photoresist was confirmed under the conditions shown in following Table 2.

[0209]

(Table 2)

Conditions for evaluating exposure resolution of positive photoresist

---

Substrate	Organic anti-reflective film: AR-19 (manufactured by Shipley Ltd.)
Thickness of resist film	300 nm

Exposure apparatus	Nikon NSR-S302 (NA 0.60, 2/3 annular)
Baking condition	PB: 110°C, 90 seconds PEB: 90°C, 60 seconds
Developing condition	NMD-3 2.38% (manufactured by Tokyo Ohka Kogyo Co. Ltd.), 30 seconds

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[0210]

The evaluation of the exposure resolution is shown in the following Table 3.

- 5 By using the positive photoresist compositions (Examples 1 to 3) including each of the resins 7 to 9 which is the specific examples of a polymer compound of the present invention, it was found that a line and space pattern of 120 nm was obtained on 1:1 and that the pattern shape showed rectangularity. The exposure in this time was 14 to 15 mJ/cm<sup>2</sup>, and the favorable sensitivity was obtained.

10 [0211]

(Table 3)

Evaluation of resolution and exposure

	Resolution (line and space)	Sensitivity (mJ/cm <sup>2</sup> )
Resin 7	120 nm	15
Resin 8	120 nm	15
Resin 9	120 nm	14

[0212]

(Example 4)

- 15 The performance of a positive photoresist was confirmed by using the resin 1 from a thickness change of a resist film when an exposure is changed. The positive photoresist composition was prepared by mixing the acid generator, the nitrogen-containing organic compound, and the solvent, each being described below.

Resin 1	100 parts by mass
Acid generator: TPS-PFBS	2.0 parts by mass
Nitrogen-containing organic compound: triisopropanolamine	0.2 parts by mass
Organic solvent: PGMEA	1250 parts by mass

As can be seen from the sensitivity profile obtained by using ArF exposure, the performance of the positive photoresist was able to be confirmed. Also, the sensitivity was favorable.

[0214]

(Examples 5 to 8)

The resolution of a positive photoresist was confirmed by using the resins 2 to 5. An ArF excimer laser was used for exposure. The positive photoresist composition was prepared by mixing each of the resins 2 to 5 with the acid generator, the nitrogen-containing organic compound, and the solvent, each being described below.

Resins 2 to 5	100 parts by mass
Acid generator: TPS-PFBS	3.0 parts by mass
Nitrogen-containing organic compound: triisopropanolamine	0.35 parts by mass
Organic solvent: PGMEA	1250 parts by mass
GBL	125 parts by mass

[0215]

“GBL” represents  $\gamma$ -butyrolactone.

The exposure resolution of the positive photoresist was confirmed under the conditions shown in following Table 4.

[0216]

(Table 4)

Substrate	Organic anti-reflective film: ARC29 (manufactured by Brewer Science Ltd.)
Thickness of resist film	300 nm
Exposure apparatus	Nikon NSR-S302 (NA 0.60, 2/3 annular)

Baking condition	PB: 110°C, 90 seconds PEB: 110°C, 90 seconds
Developing condition	NMD-3 2.38% (manufactured by Tokyo Ohka Kogyo Co. Ltd.), 60 seconds

[0217]

The evaluation of the exposure resolution is shown in the following Table 5.

By using the positive photoresist compositions (Examples 5 to 8) including the resins 2 to 5, respectively, which are the specific examples of a polymer compound of the present invention, it was found that a line and space pattern of 120 nm was obtained on 1:1 and that the pattern shape showed rectangularity. The exposure (sensitivity) in this time was shown in Table 5.

[0218]

(Table 5)

10 Resolution and exposure

	Resolution (line and space)	Sensitivity (mJ/cm <sup>2</sup> )
Resin 2	120 nm	37
Resin 3	120 nm	33
Resin 4	120 nm	37
Resin 5	120 nm	41

[0219]

(Examples 9 to 19 and Comparative examples 1 to 8)

The positive resist compositions, which have the compositions shown in following Table 6, were prepared, and then resist patterns were formed under the conditions shown in Table 7 and evaluated. The results are shown in Table 8.

15

[0220]

(Table 6)

	(A) Resin	(B) Acid generator	(D) Nitrogen-containing organic	Organic solvent
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			compound	
Example 9	Resin 11 (100 parts by mass)	PAG1 (3 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 10	Resin 11 (100 parts by mass)	PAG2 (3.4 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 11	Resin 11 (100 parts by mass)	PAG3 (5 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 12	Resin 12 (100 parts by mass)	PAG1 (3 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 13	Resin 12 (100 parts by mass)	PAG2 (3.4 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 14	Resin 12 (100 parts by mass)	PAG3 (5 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 15	Resin 13 (100 parts by mass)	PAG1 (3 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 16	Resin 13 (100 parts by mass)	PAG3 (5 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 17	Resin 14 (100 parts by mass)	PAG1 (3 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 18	Resin 14 (100 parts by mass)	PAG2 (3.4 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Example 19	Resin 14 (100 parts by mass)	PAG3 (5 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Comparative example 1	Comparative resin 1 (100 parts by mass)	PAG1 (3 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Comparative example 2	Comparative resin 1 (100 parts by mass)	PAG2 (3.4 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)



Comparative example 3	Comparative resin 1 (100 parts by mass)	PAG3 (5 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Comparative example 4	Comparative resin 2 (100 parts by mass)	PAG1 (3 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Comparative example 5	Comparative resin 2 (100 parts by mass)	PAG2 (3.4 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Comparative example 6	Comparative resin 2 (100 parts by mass)	PAG3 (5 parts by mass)	Triethanolamine (0.3 parts by weight)	PGMEA (750 parts by weight) EL (500 parts by weight)
Comparative example 7	Comparative resin 3 (100 parts by mass)	PAG1 (2 parts by mass)	Triisopropanolamine (0.1 parts by weight)	PGMEA (1150 parts by weight)
Comparative example 8	Comparative resin 4 (100 parts by mass)	PAG1 (2 parts by mass)	Triisopropanolamine (0.1 parts by weight)	PGMEA (1150 parts by weight)

[0221]

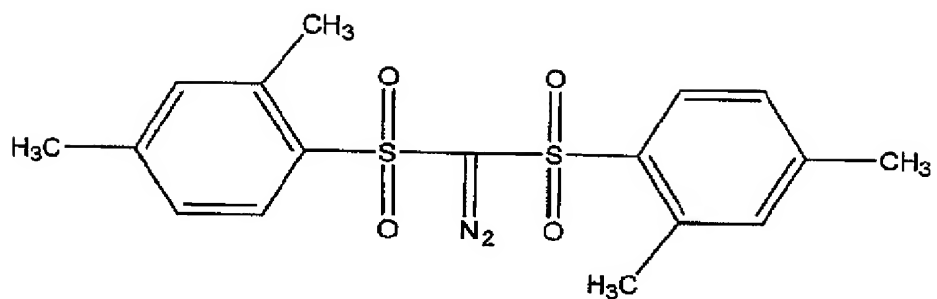
The abbreviations in Table 6 represent the following.

PAG1: triphenylsulfonium nonafluorobutanesulfonate

- 5      PAG2: bis(2,4-dimethylphenylsulfonyl)diazomethane represented by the following chemical formula (84)

[0222]

[Chem 56]



( 8 4 )

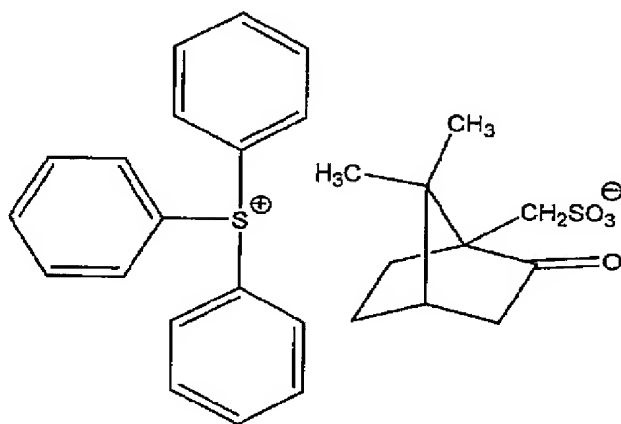
[0223]

PAG3: camphor sulfonic acid of triphenylsulfonium represented by the following chemical formula (85)

5

[0224]

[Chem 57]



( 8 5 )

[0225]

PGMEA: propylene glycol monomethyl ether acetate

10

EL: ethyl lactate

[0226]

(Table 7)

Substrate: organic anti-reflective film AR-29 (manufactured by Shipley Ltd.)

Thickness of resist film: 250 nm

Exposure apparatus: Nikon NSR-S302 (NA = 0.6, 2/3 annular)

Baking condition: PB 100°C / 90 seconds

PEB 100°C / 90 seconds

Developing condition: NMD-3 2.38% (manufactured by Tokyo Ohka Kogyo Co. Ltd.),  
23°C / 60 seconds

[0227]

The conditions for Comparative examples 7 and 8 were the same as the conditions shown in Table 2 other than changing the thickness of a resist film to 200 nm.

[0228]

(Table 8)

	Resolution (nm) line and space	Sensitivity (mJ/cm <sup>2</sup> )
Example 9	110	19
Example 10	150	54
Example 11	110	19
Example 12	110	17
Example 13	110	21
Example 14	130	10
Example 15	110	19
Example 16	110	23
Example 17	110	18
Example 18	120	28
Example 19	150	12
Comparative example 1	110	38
Comparative example 2	not resolved	—
Comparative example 3	not resolved	—
Comparative example 4	110	26
Comparative example 5	not resolved	—
Comparative example 6	170	36
Comparative example 7	not resolved	—
Comparative example 8	Thickness of the resist pattern was lost, and the pattern disappeared.	—

[0229]

When PAG2 was used, any resist pattern was not resolved in Comparative examples 2 and 5. In contrast, the resist patterns of line and space were obtained in

5 Examples 10, 13, and 18.

When PAG3 was used, any resist pattern was not resolved in Comparative example 3, and the resist pattern of line and space of 170 nm was obtained in Comparative example 6. In comparison to these Comparative examples, resolution and

sensitivity were improved in Examples 11, 14, and 19.

Line and space patterns with a line width of 120 nm and a pitch of 240 nm were formed, and in Examples 9, 12, and 15 and Comparative examples 1 and 4,  $3\sigma$  was measured, which is a measure of indicating LER. In the present Example,  $3\sigma$  was measured by the length-measuring SEM (manufactured by Hitachi Ltd., trade name: "S-9220"). The lower  $3\sigma$  means that a resist pattern with the smaller roughness and even width is obtained. The results showed that  $3\sigma$  was 6.4 nm in Example 9, 5.4 nm in Example 12, 6.9 nm in Example 15, 9.0 nm in Comparative example 1, and 6.9 nm in Comparative example 4. From these results, it was found that LER was reduced by using a structural unit (a1) of the present invention.

When PAG1 was used, resolution was about the same, whereas sensitivity was improved in Examples.

[Industrial Applicability]

[0230]

As described above, a polymer compound of the present invention is useful for formation of a fine pattern excellent in rectangularity, specifically a fine pattern for exposure of a KrF, ArF, or F<sub>2</sub> laser.

[Brief Description of the Drawings]

[0231]

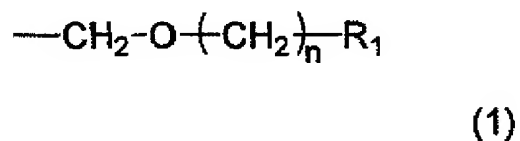
FIG. 1 is a figure showing the sensitivity profile obtained by using ArF exposure in Example 4.

[Document Type] Abstract

[Abstract]

[Problem] The present invention provides a polymer compound which can constitute a photoresist composition which is capable of having an excellent resolution, forming a fine pattern with a good rectangularity, obtaining favorable resist characteristics even when acid strength of an acid generated from an acid generator is weak, and having favorable sensitivity; a photoresist composition including the polymer compound; and a resist pattern formation method using the photoresist composition.

[Solving Means] The photoresist composition and the resist pattern formation method use the polymer compound including an alkali soluble group (i), wherein the alkali soluble group (i) is at least one substituent group selected from an alcoholic hydroxyl group, a carboxyl group, or a phenolic hydroxyl group, and the substituent group is protected by an acid dissociable, dissolution inhibiting group (ii) represented by a general formula (1):



(wherein R<sub>1</sub> represents a cycloaliphatic group which contains no more than 20 carbon atoms, and n represents 0 or an integer of 1 to 5.).

[Chosen Drawing] None

Patent Application No. 2004-134585

Information on Applicant

5 Identification Number (000220239)

1. Renewal Date August 30, 1990

(Reason) New Registration

10 Address 150, Nakamaruko, Nakahara-ku, Kawasaki-shi,  
Kanagawa-ken, Japan

Name TOKYO OHKA KOGYO CO., LTD.